Methods for Studying

Acid Precipitation in Forest Ecosystems

Institute of Terrestrial Ecology
Natural Environment Research Council
and
United Nations Educational
Scientific and Cultural Organisation

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Definitions and Research Requirements

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Compartment 126, Blackhall in Banchory Forest looking east. The River Dee is in the middle foreground. The photograph was taken by Mr. I.A. Anderson in 1972, and is reproduced by kind permission of the Forestry Commission.

The Institute of Terrestrial Ecology (*ITE*) was established in 1973, from the former Nature Conservancy's research stations and staff, joined later by the Institute of Tree Biology and the Culture Centre of Algae and Protozoa. ITE contributes to and draws upon the collective knowledge of the fourteen sister institutes which make up the *Natural Environmental Research Council,* spanning all the environmental sciences.

The Institute studies the factors determining the structure, composition and processes of land and freshwater systems, and of individual plant and animal species. It is developing a sounder scientific basis for predicting and modelling environmental trends arising from natural or man-made change. The results of this research are available to those responsible for the protection, management and wise use of our natural resources.

Nearly half of ITE's work is research commissioned by customers, such as the Nature Conservancy Council, who require information for wildlife conservation, the Forestry Commission and the Department of the Environment. The remainder is fundamental research supported by NERC.

ITE's expertise is widely used by international organisations in overseas projects and programmes of research.

Contents

A. INTRODUCTION

Several aspects of acid precipitation and its influences on terrestrial and aquatic systems have been covered at international conferences during the last 5 years, but little attention had been given to the critical evaluation of methods. To correct this deficiency, a workshop was arranged by staff of the Institute of Terrestrial Ecology (ITE). The Workshop was held in Edinburgh in September 1977, with the enthusiastic support of the United Nations Educational, Scientific and Cultural Organisation (UNESCO).

Because of the international interest in acid precipitation related to forest systems, discussion was confined to methodological problems associated with the measurement of (i) deposition of atmospheric pollutants to forest canopies and (ii) their subsequent passage to soil, essential prerequisites for the study of effects on soils.

Because of the informal nature of the Workshop, it would be inappropriate to record the full proceedings. Instead, this document gives summaries and recommendations in addition to two major invited papers dealing with (i) dry deposition and (ii) throughfall and stemflow.

Fourteen research scientists working in the U.K. were joined by a similar number of colleagues from North America and continental Europe. In total, 10 countries were represented with Dr. H.L. Teller attending on behalf of UNESCO (Appendix 1).

The five day Workshop considered three Subject Areas:

1. Evaluation of atmospheric inputs
2. Throughfall and stemflow
3. Measurement of effects.

Most time was given to the evaluation of atmospheric inputs and least to measurement of effects, before concluding with a session 'Synthesis and Implications'. A visit was made to the ITE laboratory at the Bush Estate south of Edinburgh and one day was devoted to field visits in southern Scotland. During the latter, participants saw work in progress at (i) ITE's field site (Devilla forest) where atmospheric concentrations of sulphur dioxide, ozone and oxides of nitrogen were being continuously monitored above a Scots pine *(Pinus sylvestris)* canopy, and (ii) one of the study areas of the Macaulay Institute for Soil Research, where throughfall and stemflow sampling systems were operating. At the laboratory at the Bush Estate three pieces of work were demonstrated: (a) the use of a scanning electron microscope for studying the effects of pollutants on leaf surfaces, (b) the axenic culture of clonal birch (*Betula* spp), and (c) the measurement of tree shoot extension.

Dr. M.H. Unsworth, Professor B. Ulrich and Professor K. Bjor accepted responsibility for preparing Position Papers for Subject Areas 1, 2 and 3 respectively, reviewing the existing state of knowledge and establishing a framework for stimulating discussion based on their own papers, together with shorter contributions which followed (Appendix 2). Additionally Dr. Unsworth and Professor Bjor chaired their respective Subject Areas with Dr. H.G. Miller taking charge of Subject Area 2.

The titles of all written submissions are recorded in Appendix II. Position papers for Subject Areas 1 and 2, which were clearly circumscribed, are included in this document, together with their chairmens' reports of the ensuing discussions. It was not feasible to adopt the same approach to Subject Area 3, 'Measurement of effects', which was much wider-ranging. Instead, the position paper and the debate it stimulated have been condensed into 'Perspective', the second substantive section of this report. This follows a section concerned with 'Definitions and concepts'. Because members of the Workshop were acutely aware that each tended to have his own individual understanding of different technical terms, an attempt was made to find a set of mutually acceptable and agreed definitions.

Members of the organising committee, Professors T.C. Hutchison and F.T. Last (Chairman) and Mr. I.A. Nicholson, wish to acknowledge the wholehearted commitment of the participants and their debt to Professor K. Bjor, Dr. R. Mayer, Dr. H.G. Miller, Professor B. Ulrich and Dr. M.H. Unsworth, for preparing formal papers on 'key' topics and/or chairing working sessions. Additionally they wish to thank their ITE colleagues, Dr. D. Fowler and Messrs. J.W. Kinnaird, I. Leith and I.S. Paterson, for their contributions to the organisation of the Workshop.

B. DEFINITIONS AND CONCEPTS*

by

H.G. Miller, M.H. Unsworth and D. Fowler

Meetings bringing together scientists of several disciplines usually uncover areas of confusion and conceptual misunderstanding. The Edinburgh meeting, with ecologists, foresters, micrometeorologists and physicists, was no exception, hence this attempt to provide a framework (Fig. 1) and define the main terms used in the study of acid precipitation.

Material is transferred from the atmosphere to vegetation by two mechanisms (i) sedimentation under the influence of gravity and (ii) turbulent transfer. The first mechanism applies, for example, to atmospheric precipitation (i.e. rainfall and snow) and to large solid particles (diameter$>$*c.* 20μm) in a manner independent of the nature and geometry of the receiving surface. The second mechanism allows gas molecules, small particles and drops to be transported in turbulent eddies until they are close to a surface; deposition then occurs by impaction or diffusion. This second mechanism is strongly dependent on the nature and configuration of the receiving surface.

It is conventional to divide the total input of an element or substance to an ecosystem into wet deposition and dry deposition. Sometimes these are taken to mean, respectively, the input during periods with or without measurable precipitation — an incorrect interpretation

* References to Workshop contributions are marked with asterisks*

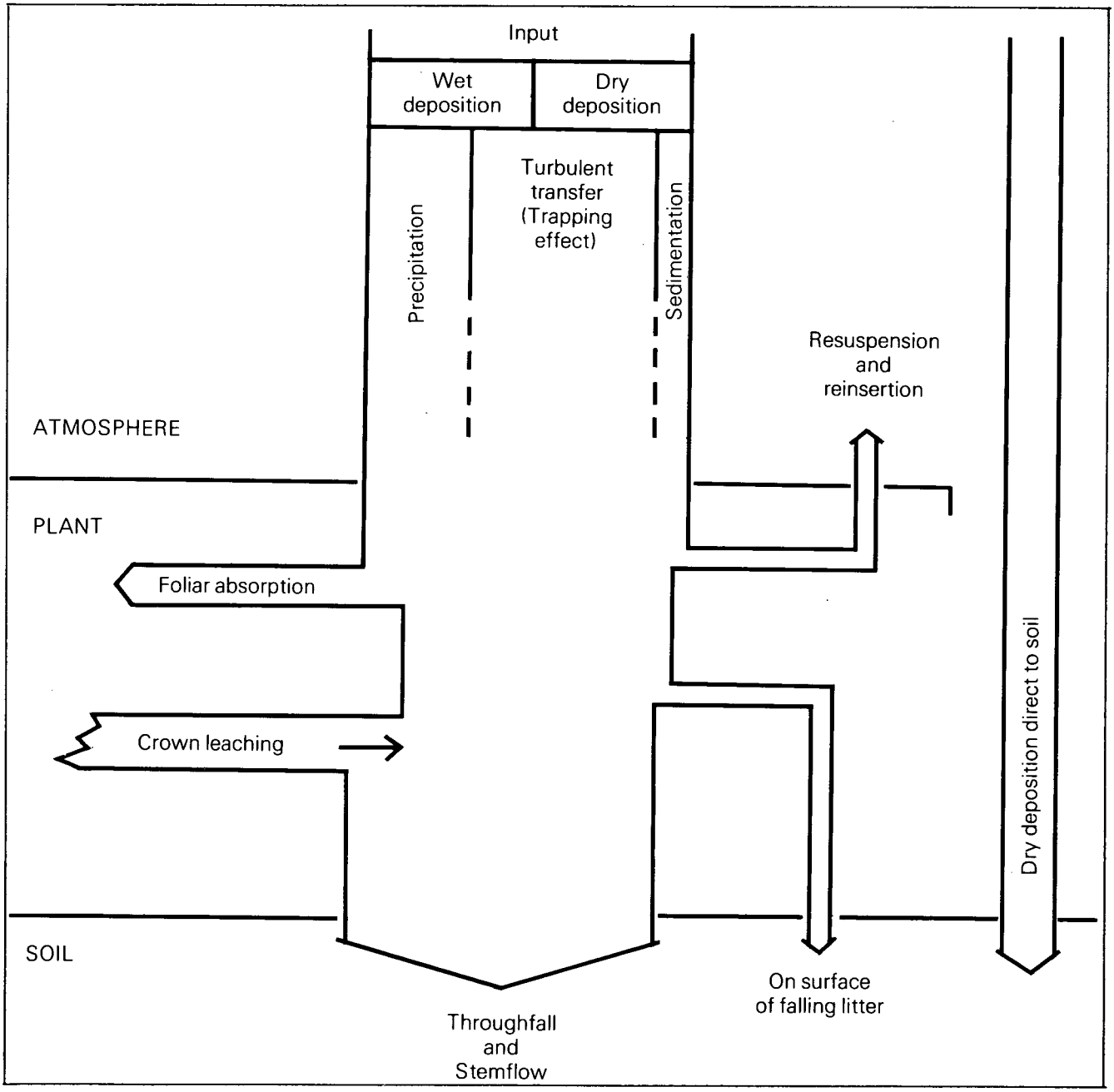

Fig. 1. Movement (pathways) of airborne substances from the atmosphere to plants and soil (after Slinn (1977) with suggestions from R. Mayer and B. Ulrich)

Wet deposition (wet precipitation) is the transfer of an element or substance from the atmosphere in aqueous solution or suspension.

Dry deposition is the direct transfer of gaseous and particulate material from the atmosphere to the surface, i.e. excluding the indirect input in aqueous solution or suspension (wet deposition). For gases and small particles (< 1 μm diameter) this transfer is effected by turbulent transfer to within a few mm of the surface and then by molecular and Brownian diffusion. Larger particles are deposited by sedimentation under the influence of gravity.

Considerable misunderstanding has been caused by the use (and misuse) of the terms wet and dry deposition, especially as they are collective terms, each embracing a number of distinct physical processes (Garland, 1978). It should be noted that the capture of gases and particles by surfaces (dry deposition) is a continuous process and so wet and dry deposition may occur simultaneously.

Precipitation input is the input of elements or substances in rain falling on horizontal surfaces. This input together with the input in trapped water droplets (*q.v.* trapping effect) comprises wet deposition. Ideally precipitation input includes only material collected by rain in clouds and as it falls through the atmosphere (Garland, 1978). In practice, however, it is difficult to avoid collection of gaseous or solid material by the sample gauge before or during rain and for this reason the total input measured by a horizontal gauge, which is the quantity measured in most studies, is better termed *bulk precipitation.*

Trapping effect is the capture from the atmosphere of an element or substance by aerodynamically rough surfaces, such as vegetation. This process is effected by turbulent transfer, impaction and diffusion. If the trapped material is a gas or dry particle then this is part of dry deposition, but if it arrives in water droplets, such as fog, drizzle or fine rain, then it is part of wet deposition. The trapping effect, therefore, is a collective term including some wet and some dry deposition processes. This has also been termed the *filtering effect* (Mayer and Ulrich, 1974), subdivided into plant filtering and soil filtering (Ulrich and Mayer*).

The capture of small water droplets by forest canopies is a particularly efficient process (Rutter, 1975; Shuttleworth, 1977). As there is a general tendency for element concentration to increase as drop size decreases, this capture results in a change of quality as well as quantity of water collected (Miller*).

Sedimentation input is the input of larger (≥ 20 μm) dry particles to a horizontal surface under the influence of gravity. This is seldom an important process unless there are nearby sources of large particles, e.g. bare soil or factory chimneys.

Gross rainfall is the amount of rainfall above a canopy of vegetation.

Net rainfall is the amount of rainfall reaching the ground beneath vegetation and is partitioned into throughfall and stemflow.

Interception loss is the difference between gross and net rainfall. This loss is assumed to have evaporated from plant surfaces.

Throughfall comprises water that (i) drips from plant surfaces (crown drip) and (ii) falls uninterrupted through gaps in the canopy (direct penetration).

Stemflow is water that reaches the ground by flowing down the surfaces of stems.

The composition of net rainfall differs considerably from that of gross rainfall. In part, this difference is attributable to increased concentrations resulting from the loss of some intercepted rain by evaporation and/or by washing previously deposited material from plant surfaces. Additionally a proportion of some elements, deposited onto plant canopies, is taken into plant tissues by foliar absorption (*cf* the uptake of solutes by roots) while other substances are lost as a result of crown leaching.

Crown leaching (canopy leaching) is the movement into aqueous solutions bathing aerial plant surfaces of (i) elements previously taken up mostly by roots and (ii) substances manufactured within the plant.

Enrichment is the concentration increase in net rainfall in comparison to gross rainfall, an increase that comes both from an increase in amount of element in net rainfall and from the decreased volume of net rainfall because of interception loss.

Gain is the increase in weight per unit ground area of an element or substance in net precipitation over the weight in gross precipitation (Miller *et al.*, 1976).

Wash-down (wash-off) is the proportion of the gain not derived from crown leaching.

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C. PERSPECTIVE*

by

F.T. Last, K. Bjor and I.A. Nicholson

Atmospheric pollution has been a cause for concern for many decades, notably in the environs of industry. Interest was heightened by the catastrophic 'smog' in London during the early 1950s, the extending loss of trees in the environs of Los Angeles and the destruction of *Pinus ponderosa* over increasing areas of southern California (Miller, 1973). The 'Los Angeles smog' is associated with the build-up of motor car exhaust fumes which are photochemically reactive. Air pollution characterised by the presence of strongly oxidising substances including ozone has become increasingly widespread but, notwithstanding, international concern has continued to be centred on sulphur pollutants, an interest that was boosted by the deliberations of the United Nations Conference on the Human Environment held in Stockholm in 1972 (Sweden, Royal Ministry for Foreign Affairs & Royal Ministry of Agriculture, 1971).

During the last few decades, many attitudes have changed. It is now widely accepted that pollutants (primary and secondary) usually occur in mixtures, although one type commonly predominates, and that the nature of these mixtures is constantly changing, partly as a result of variable inputs and differential deposition, and hence loss, of different constituents. Additionally, it is recognised that atmospheric pollutants are changed by chemical reactions, including the conversion of gaseous substances to particulate forms. The meeting in Edinburgh was held specifically to consider some consequences of one of these changes, namely that following the conversion of gaseous SO_2 to particulate sulphate (SO_4^{2-}). Although small amounts of SO_4^{2-} are 'dry deposited', much larger quantities are collected from the atmosphere and brought down by rain (precipitation). In contrast to SO_2 the deposition of sulphur pollutants as SO_4^{2-} is of relatively greater quantitative significance at sites remote from emission sources than at those nearby. Nonetheless, the dry deposition of the relatively small amounts of SO_2 reaching distant and usually rural sites, without being oxidised to SO_4^{2-} during transport, is of some importance. In the first instance, the annual accumulations of 'sulphur' even from small concentrations of SO_2 may be appreciable in terms of plant nutrition. Secondly, the deposits of SO_2 and other substances on foliage, branches and stems, together with plant leachates alter the composition of precipitation after it has been intercepted by vegetation. Thus, studies of SO_2 and SO_4^{2-} are, of necessity, inextricably linked.

Acid precipitation is not a new phenomenon, its occurrence having been noted many years ago (e.g. Gorham, 1957). But what does it do, directly and indirectly, to forest ecosystems? The chemical nature of precipitation can differ greatly at different locations and at different times of the year. Thus Bjor* indicated that SO_4^{2-} was quantitatively the most important anion in rain collected at Birkenes in southern Norway during May to June 1973, acidity being described adequately by summing sulphate and nitrate equivalents and subtracting ammonium (Semb, 1976). At the Hubbard Brook Experimental Forest, the increased input of H^+ ions in rain (precipitation) during a ten year period (1964-74) seems to have been related more to changes in NO_3^- concentrations than to those of SO_4^{2-}, which nevertheless contributed to $>$ 65% of the acidity in precipitation (Likens *et al.*, 1977). By considering H^+ ion budgets of forests, Andersson* argued that account should be taken not only of the atmospheric inputs of acids, but also of processes within the plant-soil system involving the production and consumption of H^+ ions. In so doing, he also recognised the direct toxic effects of sulphur derivatives, and, moreover, the likely benefits to be gained by plants if sulphur additions (and those of nitrogen) contributed to nutrient requirements.

Many different methods have been used, with varying degrees of success, to assess damage entirely or largely attributable to sulphur pollutants. Although needing careful interpretation because of the possible interplay with other pollutants, and with features of the physical environment, the occurrence or absence of different cryptogams including fungi (notably *Diplocarpon roseae* and *Rhytisma acerinum*), lichens and bryophytes can be used to characterise atmospheric concentrations of SO_2 from 30 to 40 $\mu g\ m^3$ to over 100 $\mu g\ m^{-3}$. The use of sensitive indicator plants has been investigated particularly in the Netherlands (Posthumus*). Thus, tobacco (*Nicotiana tabacum L.*) var. Bel W_3 characteristically develops speckled foliar necroses when exposed to ozone at concentrations $>$ 4pphm, whereas lucerne (*Medicago sativa* L.) var. de Puits develops intercostal chlorosis and necrosis in response to SO_2 fumigation. Although promising for the detection of damaging concentrations of gaseous pollutants, the use of sensitive bioindicators appears at present to be much less rewarding when dealing with acid precipitation. However, in boreal forests the rate of nitrogen fixation by nitrogen fixing lichens may provide a sensitive system for assessing acid rain effects, whereas further understanding of stress metabolism in forest trees and associated forest species may provide other ways of identifying detrimental effects (Huttunen*).

Many tests have been made with concentrations of gaseous pollutants that cause foliar blemishes and premature leaf fall, but little is known about smaller concentrations that may decrease growth without the formation of blemishes, 'chronic' by contrast to 'acute' damage. It is, however, these relatively small concentrations that are most likely to occur where acid precipitation is regarded as a potential hazard to terrestrial and aquatic systems. Whereas the decreasing growth rate of trees sited near major emission sources is reflected in narrower annual growth-rings, the use of this relatively insensitive method of assessment has not

* References to Workshop contributions are marked with asterisks *

suggested that decreased growth rates, attributable to small concentrations of pollutant, occur in the absence of blemishes. Yet, these decreased growth rates are known to occur in some crops. Aerial photographs have recorded obvious blemishes, but until now it has not been practicable with this technique to distinguish between healthy assemblages of plants and those with decreased growth rates in the absence of blemishes. However, with the diminution of locally large concentrations of SO_2 causing acute damage, pollution research should be increasingly concerned with problems of chronic damage. Furthermore, interest in direct damage should be balanced by a concern for indirect effects.

At the UN Conference held in 1972, it was suggested that acid precipitation may deleteriously affect soil fertility and hence plant productivity. The 'field' evidence from Norway, Sweden and north-east America suggests that effects on trees have not yet reached a magnitude allowing statistical substantiation, if indeed they are occurring. Nonetheless, knowing that acidity affects soils it is essential to monitor changes and to be in a position to understand their significance in terms of land capability, plant production, water quality and the survival of freshwater plants and animals.

It would be surprising if acid inputs did not affect soil processes, remembering that the 'activity' of many soil bacteria, using indices of *biomass* and/or *metabolic activity* (Ineson *et al.**), is restricted by increasing acidity. There are indications and expectations that simulated acid precipitation decreases the activity of bacteria more than that of fungi, which decreases litter decomposition and nitrogen turnover (Abrahamsen *et al.*, 1976; Tamm, 1976; Tamm *et al.*, 1976). But what is the quantitative significance of these alterations when related to the growth of over-storey and under-storey trees and groundcover, to the movement of solutes in drainage and ultimately, in extreme instances, to soil erosion as described by Freedman* in the area around Sudbury, Ontario? Whereas forest yields in non-arid temperate regions tend to be inversely proportional to the degree of acidity (Dahl and Skre, 1971) (i.e. yields decrease with increasing acidity), Benzian (1965) demonstrated that the nursery production of seedlings of many conifer species, including Norway spruce (*Picea abies*) and Sitka spruce (*Picea sitchensis*), increased as soil pH was decreased below 7.0 with the optimum for Sitka spruce being *c.* 4.5.

Soil is a complex substrate and there are surprisingly large deficiencies in our understanding of the dynamics of exchange processes between the different layers (horizons) within profiles. However, in addition to this spatial variation in a vertical plane, the distribution of stemflow and throughfall is systematically, but not uniformly, arranged in the horizontal plane. But before becoming involved with the spatially and temporally changing patterns of litter decomposition, nutrient cycling and cation exchange, it is first necessary to understand adequately the different inputs from wet and dry deposition, and how they are modified when intercepted by leaves, branches, stems and other components, including groundcover, of structured forests. There is already evidence suggesting that different plant species have different effects which conceivably differ seasonally and in different locations. To improve our understanding of the type and quantities of substances reaching soil, following the wet and dry deposition of sulphur pollutants, Dr. M.H. Unsworth and Dr. H.G. Miller have produced summaries of two sections of the Edinburgh Workshop;

(1) Evaluation of gaseous and particulate inputs from atmosphere.

(2) Throughfall, stemflow, crown leaching and wet deposition.

In developing their critiques they have identified the facets which members of the Workshop considered to be of priority. It is hoped that the data obtained will facilitate a more informed approach to the study of effects on interrelated soil processes affecting:

(i) plant nutrition,

(ii) the nature of run-off and drainage from catchments and hence of effects on aquatic plants and animals, and

(iii) the conservation of soil resources.

The Workshop also recognised that there was a need to seek further observations on the transfer of atmospheric pollutants to snow, and on their subsequent movement in snow-melt.

Having examined the nature of the inputs, it would seem appropriate to debate, at a future Workshop, the different conceptual approaches that could be considered for examining the effects of differing inputs on complexes of soil processes and, in so doing, extend knowledge of sulphur pathways and of biogeochemical cycling processes in ecosystems. Dr. Andersson* emphasised the importance of investigating complete ecosystems, illustrating his approach with (i) a hydrogen ion budget and (ii) a nitrogen-dependent production model for forest trees, the latter recognising that acidity may deleteriously influence tree growth by minimizing nitrogen transformations, and hence availability, in soils.

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D. SUBJECT AREA: EVALUATION OF ATMOSPHERIC INPUTS*

I. DRY DEPOSITION OF GASES AND PARTICLES ONTO VEGETATION: A REVIEW

by

M.H. Unsworth

It may seem illogical to begin a consideration of acid precipitation by discussing input processes which specifically exclude precipitation, but in recent years, it has become increasingly recognised that dry deposition is a particularly efficient process for removing sulphur dioxide and certain other gases from polluted air masses (Granat *et al.*, 1976; Garland and Branson, 1976). The net effects of dry deposition depend partly on the quantities of materials deposited, and partly on how these materials interact with vegetation and soils and also with precipitation.

Two groups of substances can be classified by their chemical and physical properties:

(i) materials which, when deposited on vegetation or removed by precipitation, cause acidity, and

(ii) materials which indirectly influence acidity, for example by controlling the rate at which materials in category (i) are deposited or, alternatively, by having chemically or physiologically protecting effects.

The first group includes important substances such as sulphur dioxide, oxides of nitrogen, sulphate and nitrate particles, and droplets of sulphuric and nitric acids. Substances in the second category are less easily defined, but include ammonia, which by its influence on the pH of dew and rain may influence the dry deposition of SO_2 to wet canopies (Fowler and Unsworth, 1974), and ozone, which induces stomatal closure in some plant species (Hill and Littlefield, 1969).

Fluxes of particulate pollutants to canopies have seldom been measured in the field and calculations are usually based on results of laboratory experiments (Chamberlain, 1975*a*). In contrast, considerable progress has been made in recent years in the measurement of fluxes of gaseous SO_2 and O_3 to crops and soils (Chamberlain, 1975*b*), but forests continue to pose problems which are discussed later. However, our recently acquired knowledge of forest micrometeorology and our understanding of pollutant uptake by shorter vegetation, enables intelligent guesses to be made about the uptake of pollutants by forests. For this reason, it is useful to review some of the physical principles relevant to gas exchanges between surfaces and the atmosphere, and to consider schemes for interpreting flux measurements, including the calculation of V_g, the deposition velocity or ratio of flux to concentration (at a specified height). While of undoubted use when describing fluxes of particles (Chamberlain, 1955), it seems that insufficient information is available for the concept to be used to predict gaseous deposition to forests.

* References to Workshop contributions are marked with asterisks*

1. MICROMETEOROLOGICAL MEASUREMENT OF GASEOUS FLUXES

(a) Physical principles

The principles of micrometeorological methods of flux measurements (e.g. reviewed by Thom, 1975) are well established and have been used often over a variety of short crops to measure evaporation and photosynthesis, and, less often, to measure pollutant uptake; there have been few studies over forests. Two techniques are commonly employed, flux-gradient and eddy correlation. Both are theoretically applicable only where canopies are extensive, horizontal and uniform, and when temporal changes of concentrations are relatively small during periods of observation (Unsworth and Fowler, 1976; Garland, 1977).

(1) Flux-gradient methods

Flux density F is proportional to the vertical gradient of concentration $\delta x/\delta z$, the constant of proportionality being the eddy diffusivity K, thus

$$F = -K\,\delta x/\delta z \qquad (1)$$

(Downward fluxes are negative by convention)

Although the minimum number of measurements defining $\delta x/\delta z$ is two, in practice more levels are often used to increase accuracy (Garland *et al.*, 1973; Biscoe *et al.*, 1975). Eddy diffusivity K, Eq. 1, is estimated assuming that the mechanisms transporting momentum, heat and mass in turbulent flow are similar.

Two methods are commonly used; the first (the energy balance or Bowen ratio method) recognises that, for all atmospheric stabilities, the diffusivities for heat, gases and water vapour may be assumed to be identical. When the energy balance is applied (e.g. Monteith, 1973).

$$K = -H/(\rho c_p\,\delta\theta/\delta z) \qquad (2)$$

where H is the available energy (net radiation minus storage terms), ρc_p is the volumetric specific heat of air and θ is the equivalent temperature defined by $\theta = T + (e/\gamma)$ with T, air temperature (K), e, vapour pressure and γ the psychrometric constant. Substituting in Eq. 1 for K gives

$$F = H\,(\delta x/\delta\theta)/\rho c_p \qquad (3)$$

The second method of estimating K (the aerodynamic method) uses empirical relationships between diffusivity for momentum K_M, calculated from wind and temperature profiles over a canopy, and the diffusivity K for pollutants. The resulting generalised equation for pollution flux is

$$F = -k^2(z-d)^2\,\frac{\delta u}{\delta z}\,\frac{\delta x}{\delta z}\,f \qquad (4)$$

where k is von Karman's constant (0.41), d is the zero plane displacement for momentum, u is horizontal wind speed and f is an empirical stability factor (Stewart and Thom, 1973). The variation of f with stability over bare ground and short crops is well established (e.g. Thom, 1975). However the use of 'short crop' values of f when calculating evaporation over forests (Thom *et al.*, 1975 ; Sinclair, private communication; James, 1977) leads to the production of under-estimates; Mukammal *et al.* (1966) came to a similar conclusion when working with maize. For example, Thom *et al.* (1975) found that f was about 2.5 in neutral conditions whereas the accepted value is unity over short crops. There is no theoretical explanation of this discrepancy.

Thus, the aerodynamic method may lead to large uncertainties in fluxes measured over forests or tall, rough crops unless the stability factor can be checked by independent measurements. Over shorter crops, or bare soil, it is an attractive method because gradients of wind speed and temperature can be measured quite precisely. The method is applicable by day and night, providing that wind speeds are never less than 1 m s^{-1}.

The Bowen ratio method has a sounder theoretical basis at all stabilities, but requires more measurements (*viz.* net radiation, soil heat flux, humidity and temperature gradients in addition to pollutant gradients) and may not be used when net radiation values are small, for example at night and when the sun is low or even on heavily overcast days.

In the boundary layer above forests, eddy diffusivities are typically 1 to 10 m^2 s^{-1}. For an SO_2 flux of 0.2 μg m^{-2} s^{-1} (e.g. corresponding to deposition velocity of 1 cm s^{-1} and concentration of 20 μg m^{-3}), Eq. 1 suggests that SO_2 gradients would be in the range 0.02 to 0.2 μg m^{-3}/m, a range posing severe methodological problems if flux is to be deduced accurately from gradients.

(2) Eddy correlation

This method, recently reviewed by Dyer (1975) and Kaimal (1975), measures flux directly by recording the mean product of (i) fluctuations in gas concentration χ' and (ii) vertical wind speed w', i.e.

$$F = \overline{\chi' w'} \qquad (5)$$

To measure all eddies, it is necessary to have fast response sensors. However, errors from sensors with inadequate responses are less over rough surfaces (e.g. forests) than smooth surfaces. Thus simple propellor wind sensors under-estimate fluxes by only 10 to 20% over forests, but by up to 40% over short crops (Moore, 1976). Fluctuations in gas concentrations χ'are similar in scale to gradients of $\delta\chi/\delta z$. For this reason it is necessary to have sensitive instruments for measuring gas concentrations, but a high degree of instrument stability is less important for eddy correlations than when exploiting gradient methods. With simple eddy-correlation systems, the errors in assessing fluxes may be appreciable if the w' anemometer is not held strictly vertical or if the mean air flow above the canopy is not horizontal, as at sloping sites. It is also essential that samples are taken from positions characteristic of the whole canopy.

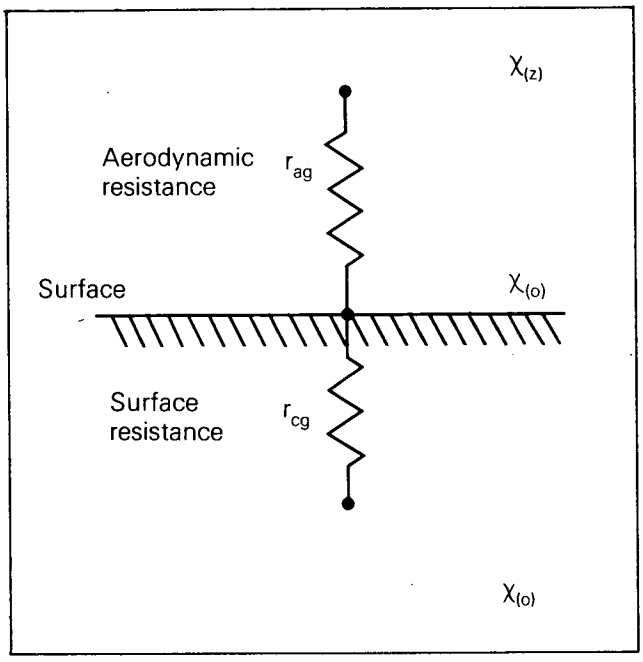

Fig. 2. A resistance analogue describing the transfer of pollutants to, and their destruction at a surface

(b) Interpretation of fluxes

Measurements of pollutant fluxes are difficult to obtain and are unlikely to be made (i) at many sites or (ii) over long periods. However, progress can be made if factors controlling fluxes can be identified and predicted. At its simplest, flux is interpreted as equivalent to deposition velocity V_g .

$$V_{g(z)} = F/\chi_{(z)} \qquad (6)$$

but the use of deposition velocity necessitates a gross simplification of the factors controlling pollutant uptake. This being so, it can only be recommended when it is known either that a constant value of V_g is appropriate, or when variations of flux and concentration with time are known sufficiently well to define a mean value of V_g. Nevertheless, V_g is a useful parameter for modelling transport on a regional scale (Fisher, 1975), but it may introduce large errors when used to estimate fluxes to individual crops or ecosystems, especially over short periods of time. In these instances, resistance analogues (Monteith, 1973) are of value because they separate restrictions on transfer imposed by the atmosphere from those imposed by surface factors. In the simplest resistance analogue, the aerodynamic resistance r_{ag} determines the flux of pollutant from concentration ('potential') $\chi_{(z)}$ in air above the surface to 'potential' $\chi_{(o)}$ at the surface (Fig. 2). Ohm's Law gives

$$F = \frac{\chi_{(z)} - \chi_{(o)}}{r_{ag}} \qquad (7)$$

Similarly, the rate of destruction of the pollutant at the surface is described by

$$F = \frac{\chi_{(o)} - O}{r_{cg}} \qquad (8)$$

where r_{cg} is the surface resistance. Combining Eqs 7 and 8 to eliminate the usually unobservable concentration $\chi_{(o)}$ gives

$$F = \frac{\chi_{(z)}}{r_{ag} + r_{cg}} \qquad (9)$$

showing that

$$V_g = (r_{ag} + r_{cg})^{-1}$$

For canopies of plant assemblages a similar form of analysis may be used by assuming that the transfer is to an imaginary surface within the canopy at which the 'sinks' are concentrated. In such instances r_{ag} can be treated as the sum of two resistances, one identical to that for momentum r_{am} and the second a bluff-body resistance r_{bg} (Monteith, 1973). The value of r_{am} can be estimated from analyses of wind profiles above the canopy as illustrated in Fig. 3 which shows, for a neutral atmosphere, hypothetical values of wind speed and gas concentration plotted on a logarithmic scale against height above the zero plane. At a height $z - d = z_o$ there is an apparent sink for momentum, and the aerodynamic resistance for momentum transfer r_{am} equations for estimating r_{bg} were reviewed by Garland (1977); a useful approach described by Thom (1975, Eq. 109, p.93) calculates r_{bg} from micrometeorological measurements above crop canopies which are thoroughly wet with rain. In principle r_{ag} has a third component, associated with the difference in sink levels for gas and momentum, but analysis by Stewart and Thom (1973) shows that, for forests, this component is an order of magnitude smaller than r_{am} or r_{bg}.

The sizes of surface resistances r_{cg} depend on the paths and mechanisms of pollutant deposition. Unsworth *et al.* (1976) reviewed the principles of transfer of SO_2 to leaves, in comparison with the processes of transpiration and photosynthesis. If transfer of SO_2 was only to substomatal cavities, assumed to be perfect sinks, the resistance r_{cg} would be proportional to the (measurable) stomatal resistance for water vapour diffusion r_s, the

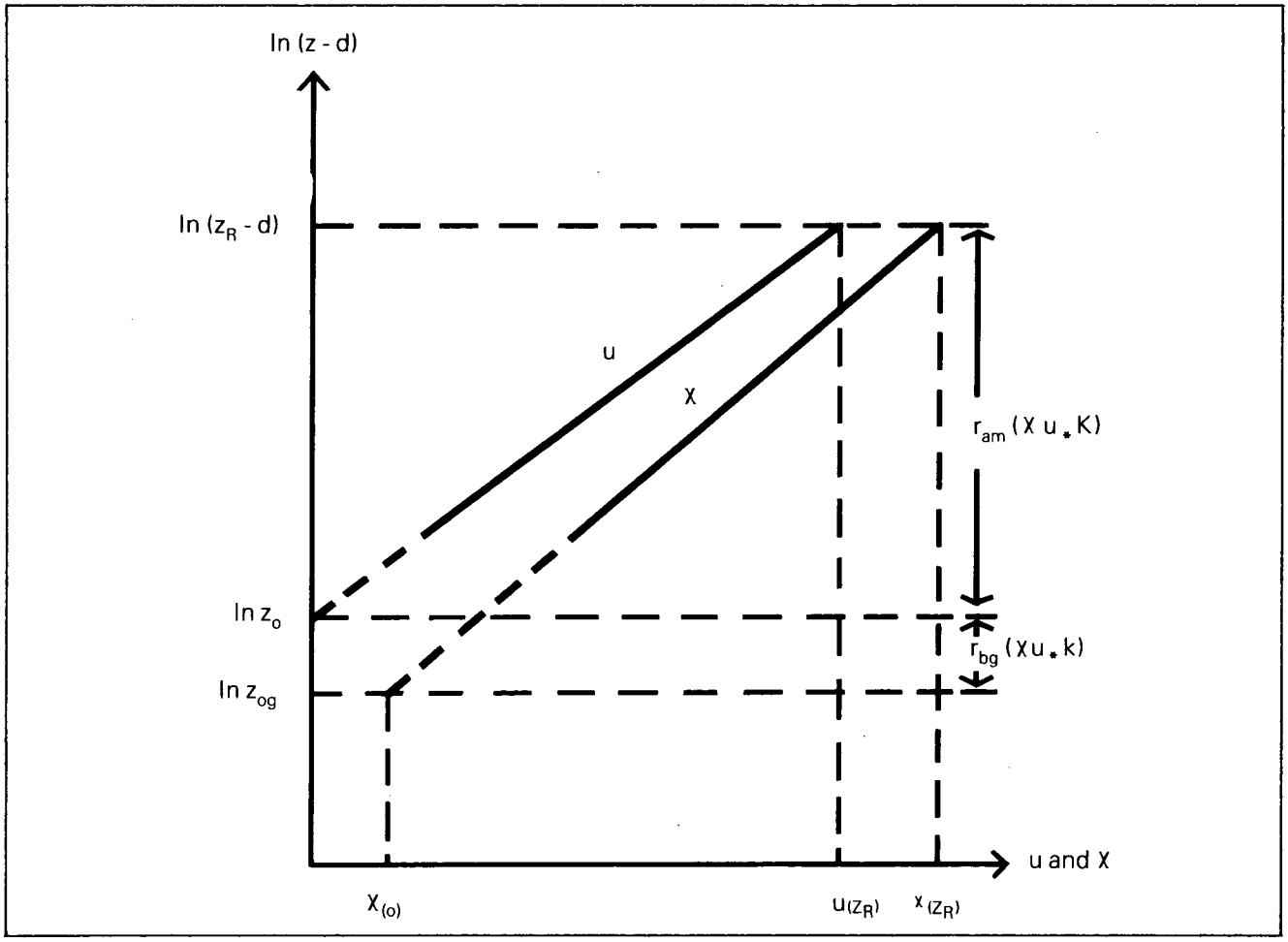

Fig. 3. Graphical representation of the meaning of components r_{am} and r_{bg} of the aerodynamic resistance r_{ag} to gas transfer. Hypothetical values of wind speed u and pollutant concentration χ are plotted against the logarithm of height above the canopy zero plane. The extrapolated wind speed is zero at $z - d = z_o$, defining the sink for momentum. The extrapolated concentration has value $\chi_{(o)}$ at $z - d = z_{og}$ where $\chi_{(o)}$ is the apparent surface concentration. Resistances r_{am} and r_{bg} are proportional to $\ln (z_R - d) / z_o)$ and $\ln z_o/z_{og})$ respectively (see Monteith, 1973, pp. 196 - 199).

from reference height z_R to $z_o + d$ is given by

$$r_{am} = u(z_R)/ u_*^2 \qquad (10)$$

where u_* is the friction velocity, found from the wind profile. There is an additional resistance r_{bg} for mass transfer, corresponding to a lower apparent sink at height $z_{og} + d$. Values of r_{bg} depend on wind speed, roughness and molecular diffusivity. Empirical coefficient of proportionality being the ratio of the molecular diffusion coefficients

$$D_{SO_2}/D_{H_2O} \simeq 2$$

Similarly, the resistance r_c to water vapour diffusion of a crop canopy, leaf area index L, can often be equated to r_s/L (Monteith, 1973; Tan and Black, 1976) and, for the ideal situation, the canopy resistance to SO_2 uptake

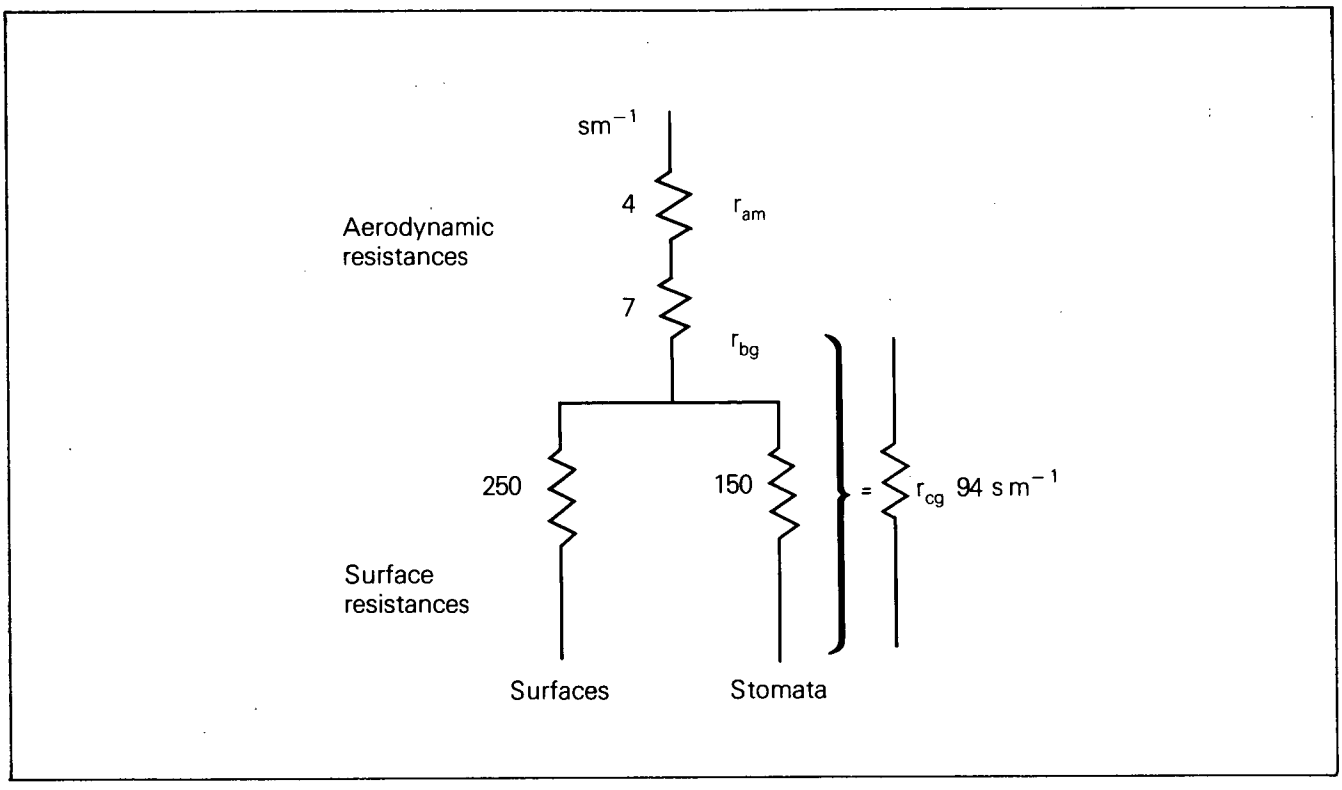

Fig. 4. A resistance analogue of transfer to a forest with resistances likely to be encountered at noon on a fine summer day (after Stewart and Thom (1973) and Fowler (1976)). The value of V_g is $(94 + 4 + 7)^{-1}$ m s^{-1} = 0.95 cm s^{-1}

would then be known. In general, however, leaves and canopies have additional paths for removing SO_2, on cuticles, bark, stems etc., and these may be regarded as additional resistances in parallel with the stomatal resistance (Fig. 4). These resistances differ for different pollutants and may be variable in space and time; little is known of them at present.

The role of the different resistances in controlling fluxes (or determining V_g) suggests that if one is small it may effectively short-circuit others. Thus if surface resistances are sufficiently small, atmospheric factors are the major limitation to disposition (Fig. 4). In contrast, if surface resistances are very large, fluxes are determined almost entirely by concentration and surface resistance, independent of wind speed or surface roughness. If stomatal resistances for water vapour transfer are known, the uptake of pollutants through stomata may be calculated, but in general stomatal uptake will be less than canopy uptake.

(c) Results of micrometeorological measurements

(1) Sulphur dioxide

Sulphur dioxide appears to be the only gaseous pollutant of direct significance to ecosystem acidification, and for which atmospheric fluxes have been measured. In most instances concentrations of SO_2 have been measured with the wet chemical method developed at Harwell and described by Atkins and Garland (1974). However, in recent years, gas analysers have been used increasingly for gradient analyses, and, in this context, the chemiluminescent technique of Stauff and Jaeschke (1975) appears to be potentially very sensitive.

Garland (1977) reviewed his own measurements and tabulated values of r_{ag} and r_{cg} (deduced as a residual from Eq. 9). He concluded that:

(i) for short grass r_{ag} was larger than r_{cg},

(ii) for long grass r_{cg} was larger than r_{ag},

(iii) for bare calcareous soil r_{cg} was insignificantly different from zero, and

(iv) for fresh water r_{cg} was sometimes very small and sometimes large, the changeover appearing to occur rapidly.

Other measurements, using the aerodynamic gradient method by Whelpdale and Shaw (1974) (over water), Shepherd (1974) (over grass), Fowler and Unsworth (1974) (over wheat) and Fowler (1976) (wheat and bare soil), have given reasonably consistent values enabling Garland (1977) to conclude that an appropriate annual mean deposition velocity for all surfaces (including urban areas and forests) would be about 0.85 cm s^{-1}. However, this average is based on a small number of flux measurements which may be biased by season and daylight hours, and is derived after making some intuitive assumptions about the sink strength of unknown surfaces. Nevertheless, the value is probably the best estimate to date for regional studies, and appears to be consistent with other observations of regional mass balance (Smith and Jeffrey, 1975).

In his micrometeorological study of SO_2 deposition to a wheat canopy over two seasons, Fowler (1976) found that r_{cg} was influenced by weather, time of day and season. He was able to deduce the separate stomatal and surface contributions to r_{cg} and hence to model sulphur deposition to crop canopies. His method of analysis enabled him to calculate V_g, the estimates obtained closely agreeing with others already published. His measurements showed for the first time that r_{cg} is very small when crops are wet with dew. A few measurements showed that r_{cg} was also small during rain, but more measurements are necessary to confirm this important finding. In contrast, when the crop was dry and foliage senescent r_{cg} was very large. Thus, the value of V_g for SO_2 to the crop varied considerably diurnally and seasonally, indicating that the use of long-term figures for deposition velocity may be misleading.

(2) Other gases

Söderlund and Svensson (1976), interested in NO_x, assumed a deposition velocity similar to that of SO_2, but without supporting evidence. Dry deposition of ammonia may be rapid because it is very soluble: its transfer to wet and dry canopies may parallel that of SO_2. The 'deposition' of ozone varies greatly both diurnally and seasonally, possibly because it is only taken up through stomata (Rich *et al.*, 1970).

2. OTHER METHODS OF MEASURING GASEOUS UPTAKE

(a) Wash off and/or vegetation analysis

Sulphur loosely held on surfaces of leaves may be analysed in leaf washings whereas amounts actually absorbed can be estimated only when foliage is destructively sampled. But, of course, allowances must be made for sulphur taken up by roots, some of which is also ultimately leached from foliage (Raybould *et al.*, 1977).

(b) Tracer methods

When plants are exposed to gaseous $^{35}SO_2$, it is possible to measure foliar uptake and to distinguish atmospheric from soil-derived sulphur. However the use of tracers in field experiments was found by Garland *et al.*, (1973), and Owers and Powell (1974) to be of restricted value because of environmental contamination, a limitation of less significance when leaves and shoots exposed to $^{35}SO_2$ are confined in cuvettes (Garland*). The latter procedure enables components of surface resistance (r_{cg}) to be studied.

(c) Mass balance

The uptake of SO_2 on container walls needs to be minimised, a difficult problem in humid conditions (Spedding, 1969). Payrissat and Beilke (1975) measured the rate of removal of SO_2 from an enclosure containing soil samples and were able to deduce its deposition velocity to soil. In the same way, Turner *et al.* (1973) measured the uptake of ozone by soil.

3. FLUXES OF SO_2 TO FORESTS

When forest canopies are dry, their canopy resistances r_{cg} are very large compared with r_{ag}, the aerodynamic resistance. If stomata are the main sinks for SO_2, as Garland (1977) found, then reasonable estimates of the uptake of SO_2 by coniferous forests can be obtained from data reviewed by Jarvis *et al.* (1976). In this way, deposition velocities seem to range from 0.2 to 1 cm s^{-1} However, this approach is less applicable to the problems of deciduous forests (Rauner, 1976). Less is known of the origins of the non-stomatal component of dry-surface resistance identified in wheat by Fowler (1976). This deficiency, which might be corrected using cuvettes, prevents the rational estimation of SO_2 fluxes to dry canopies.

When canopies are wet with dew or rain, their resistances r_{cg} are greatly decreased. In these conditions the aerodynamic resistance r_{ag} is likely to be significant but, because r_{ag} over forests is always relatively small, SO_2 fluxes to wet canopies are, at least initially, probably an order of magnitude larger than those to dry canopies (i.e. $V_g \simeq 10$ cm s^{-1}). For these conditions it is important to obtain accurate estimates of r_{ag}. However, in wet conditions, surface resistances probably increase with time as surface films become more acid as a result of SO_2 fluxes, but little is known as yet about surface chemistry and its effects on the absorption of gaseous SO_2. Knowledge of evaporation from wet canopies may be adequate, but does the composition of shrinking drops influence rates of evaporation?

In summary, the annual deposition of SO_2 to forests in high rainfall areas depends mainly on (i) aerodynamic factors, (ii) the chemistry of rain and dew, and (iii) the surface chemistry of aerial plant structures. Additionally, the frequency of rainfall and the extent of canopy wetness are important. In forests in dry areas, the annual deposition of SO_2 is largely controlled by surface resistances, seemingly including a large stomatal component.

4. DRY DEPOSITION OF PARTICLES AND DROPLETS

Sedimentation and turbulent impaction are the principle mechanisms for the dry deposition of non-gaseous materials, with the former being negligible except when there are nearby sources of large particles, or when particles may grow by aggregation or condensation (Chamberlain, 1975*a*; Fuchs, 1964). Theoretically, impaction efficiencies depend on particle size and mass, wind speed and obstacle (trapping surface) size. In practice, dry particles (but not droplets) tend to bounce from smooth surfaces, so decreasing impaction efficiencies. White and Turner (1970) found that hairy leaves (hazel) trapped salt spray less efficiently than smooth leaves at low wind speeds; on the other hand, hairy leaves may trap solid particles more efficiently than smooth leaves (Chamberlain, 1975*a*). The small diameter needles of conifers trap fog efficiently. Shuttleworth (1977) has recently described theoretically the capture of fog by forests in terms of resistance analogues.

Theoretical calculations and laboratory measurements of particles ranging from 0.1 to 1 μm (typical of atmospheric aerosols in dry air) suggest deposition velocities onto vegetation and soil of only 10^{-2} to 10^{-1} cm s^{-1} (Chamberlain, 1975*a*). Because these values are

small compared with the rates of (i) the removal of atmospheric aerosols by rain and (ii) dry deposition of SO_2 (Granat *et al,* 1976), the dry deposition of aerosols is often neglected in regional and global sulphur budgets. However, inputs of particles to forest ecosystems may not always be negligible for several reasons:-

(i) Particulates may be the main form of airborne pollution at large distances from industrial sources.

(ii) The validity of theoretical values of V_g is sometimes questionable. Wesely *et al.* (1977) reported deposition velocities as large as 1 cm s^{-1} for aerosols in the diameter range 0.1 to 1 μm when working in the field with 'short' grass. They also cite papers by Peirson *et al.* (1973) and Sehmel and Hodgson (1976) which support their results.

(iii) Deposition is strongly dependent on particle sizes and wind speeds. Hygroscopic particles such as ammonium sulphate may grow when relative humidity is below 100% (Garland, 1969). If they enlarge to 10 μm, particles characteristic of fog, then their deposition velocity to short grass would exceed 2 cm s^{-1} (Chamberlain, 1975*b*).

(iv) The 'rough' structure of forests and the frequent high speeds of associated winds combine to increase the collection efficiencies of forests compared with those of short vegetation.

Thus, in areas where low cloud is common (e.g. coastal regions and hills), capture of droplets of wind-blown fog *in the absence of precipitation* may be an important chemical input, although it is of little hydrological significance and has seldom been studied. Chamberlain (1975*a*) deduced from measurements by Huzioka *et al.* (1953) that the deposition velocity for fog to a coniferous forest was about 20 cm s^{-1}. Taking a fog water content of 0.25 g m^{-3} (Roach *et al.*, 1976) and a sulphate concentration of 5 mg l^{-1} (Junge, 1963), Chamberlain developed his calculations to indicate a sulphate input of about 20 mg sulphate m^{-2} day^{-1} comparable with the 50 mg l^{-1} in sea fogs reported by Junge, (1963). Thus, it appears that, in forests in foggy areas, annual inputs of sulphate in fog may be 1 to 2 g m^{-2} $year^{-1}$, an amount comparable with that attributable to rainfall (Dovland *et al.*, 1976). It should be remembered that the contributions of fog would *not* be measured by equipment currently used in most precipitation networks.

In dry conditions, and assuming a deposition velocity of 0.1 cm s^{-1} for sulphate aerosols, it has been estimated that *c.* 1 mg sulphate m^{-2} day^{-1} would be deposited in afforested areas if the aerosol contained 10 μg sulphate m^{-3}. These amounts are probably much smaller than those attributable to the turbulent impaction of droplets formed around particles.

5. GENERAL CONCLUSIONS AND SUMMARY

When forest canopies are dry, the rates of sulphur dioxide deposition depend primarily on surface resistances and on atmospheric concentrations. Surface resistances for some tree species appear to equate closely with stomatal resistance, and, if this is so, estimates of SO_2 uptake may be made quite accurately from bulk canopy resistances derived from recent micrometeorological studies of forest evaporation. The existence, nature and magnitude of other surface resistances, associated with cuticle, stem and bark, need further investigation.

When canopies are wet, deposition is largely determined, at least initially, by aerodynamic resistances which, in any event, are comparatively small; their importance in stable conditions e.g. when dew is forming, needs to be elucidated.

Micrometeorological techniques e.g. the use of fluxatrons, may enable our knowledge and understanding of SO_2 fluxes to be greatly extended but their use necessitates a willingness to use sophisticated instruments.

With the increasing 'uptake' of SO_2 in wet conditions, surface resistances probably increase. In the event, our understanding of surface phenomena is restricted by an inadequate knowledge of surface chemistry. Rates of drying, after both rain or dew, may have an important effect on the amounts of dry deposition to wet canopies, and, thus, precipitation *frequency* may prove to be more important than *quantity*. Dry particles seem to be inefficiently trapped by forests, but there are a few disquieting contradictions in the literature. In humid conditions, and in mist and fog, particles probably grow such that their impaction efficiencies, to forests, are increased by an order of magnitude. In these circumstances they would be trapped by forest trees but not by standard raingauges which, in this respect, are inefficent. Crude calculations suggest that fog droplets may be important sources of different ions in coastal and hilly regions. The biological consequences of the 'slow' evaporation of acidic fog droplets, trapped on leaves, need investigation.

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D. SUBJECT AREA: EVALUATION OF ATMOSPHERIC INPUTS*
II. EVALUATION OF GASEOUS AND PARTICULATE INPUTS FROM THE ATMOSPHERE: CHAIRMAN'S REPORT AND RECOMMENDATIONS

by
M.H. Unsworth

Discussions were concerned with inputs of gases and particles to forest ecosystems. It soon became clear that techniques for studying the inputs could be divided into methods appropriate for short-and long-term assesments. The former had been used by a number of participants for the study of mechanisms affecting inputs, in particular the effieciency of the atmosphere in transporting material to vegetation and the efficiency of vegetation in removing material from the air. At the Workshop, the use of resistance analogues for interpreting measurements and separating atmospheric from surface effects was debated (e.g. Fowler*; Garland*; Stewart*).

To interpret effects on ecosystems, it is usually necessary to have knowledge of pollutant inputs over long periods, but the necessary integration from short- to long-term has seldom been made. In principle, if the mechanisms determining inputs are thoroughly understood, long-term inputs could be predicted from quite simple data, perhaps concentrations and weather records, combined with details of ecosystem components. In practice, however, and in the present state of knowledge, it seems better to make series of short-term measurements, as a reliable long-term method of monitoring is not available.

1. SHORT-TERM METHODS

(a) Gases

(1) Micrometeorological

Micrometeorological methods enable inputs entering canopies to be deduced from measurements made in the boundary layer of air usually extending a few metres above the canopy. General introductory reviews of the methods have been prepared by Denmead and McIlroy (1971), Monteith (1973) and Thom (1975). Micrometeorological methods are advantageous because they (i) do not necessitate destructive sampling and (ii) enable repeated assessments at intervals as short as 30 minutes. On the other hand, they necessitate complex instruments and are only applicable to extensive, horizontal and homogeneous canopies.

There are three micrometeorological methods for measuring the flux densities of pollutants to canopies (flux density = mass per unit ground area per unit time).

(i) *Aerodynamic method:* this requires measurements of wind speed, temperature and gas concentration gradients above the canopy. It has been used widely and successfully for measuring gas and water vapour fluxes over short crops (Biscoe *et al.*, 1975; Denmead, 1976; Ripley and Redmann, 1976). However, it has become clear in recent years that substantial underestimates (by a factor of two or three) may occur if the aerodynamic method is used over the rough surfaces of tall crops, including forests (Mukammal *et al.*, 1966; Thom *et al.*, 1975; Jarvis *et al.*, 1976). An empirical correction factor, given by Thom *et al.* for a pine forest, may be applied, but, until the basis for this correction is fully understood, it is preferable to use other methods when studying forests.

When working with air pollutants, the limiting factor in applying the aerodynamic method is usually the precision required in determining gradients of gas concentrations. Suitable methods have been developed with SO_2 (Fowler and Unsworth, 1974; Garland, 1977), ozone (Galbally, 1971; Turner *et al.*, 1974) and ammonia (Denmead *et al.*, 1974) using either wet chemistry or commercial gas analysers. Over forests, the rough surface leads to concentration gradients one or two orders of magnitude smaller than over short vegetation for the same flux densities, and at present analytical methods are not sufficiently sensitive to deduce pollutant fluxes to forests by the aerodynamic method, although an upper limit of flux may be estimated (Garland, 1977).

(ii) *Energy balance method:* this depends on measurements of gradients of gas concentration, temperature and humidity and of the available energy (net radiation minus storage terms) at the canopy.

The method works well over short and tall vegetation (Biscoe *et al.*, 1975; Jarvis *et al.*, 1976) when there is adequate available energy but is inaccurate when little energy is available, for example, at night, under heavily overcast skies, or when solar elevation is low. Because of these reservations and the need for more instruments, this method has been used less than the aerodynamic method for air pollution work. Denmead *et al.*, (1974) used the method to measure ammonia fluxes from pasture; Turner *et al.*, (1974) calculated ozone fluxes to maize by comparison with evaporation measured by the energy balance method, and Leuning *et al.*, (1979) used the method for measuring ozone fluxes to tobacco.

(iii) *Eddy correlation method:* in this method fluxes are measured directly by correlating vertical velo-

* References to Workshop contributions are marked with askerisks*

cities of turbulent eddies with the concentrations of gases in the eddies. The method requires sophisticated instruments for detecting very rapid changes in concentrations and for recording and analysing these changes. Fluxes of heat and water vapour over forests have been reported (Hicks *et al.*, 1975; Moore, 1976) and a novel system for CO_2 fluxes was described by Desjardins (1974). Relatively simple 'Gill' propeller anemometers give usable measurements of wind speed fluctuations a few metres over forests (Stewart*), but are subject to larger errors over smooth crops (McBean, 1972). At the Workshop, Galbally* and Garland* reported measurements of SO_2 fluxes to a pine forest by eddy correlation using a Gill anemometer and an experimental fast-response flame photometric SO_2 analyser. Wesely *et al.*, (1978) have used eddy correlation to measure ozone fluxes to maize.

In general, eddy correlation is an attractive method for use over forests if instruments can be developed. The development of a low-cost sonic anemometer (Campbell and Unsworth, *in prep.*) removes the restrictions applying to the use of Gill anemometers, but there remains a need for gas analysers with fast time responses for pollutants. The method is particularly sensitive to (a) canopy irregularities and (b) non-horizontal wind.

(2) Deposition of atmospheric tracers

After exposing vegetation to known concentrations of an atmospheric tracer for measured periods, inputs can be assessed from the analysis of vegetation. However, care must be taken to ensure that tracers have the same deposition rates as normal pollutants; further, concentrations of tracers must not trigger uncharacteristic physiological responses. The use of radioactive isotopes enables sensitive and relatively simple analyses, but contaminating residues restrict repetition. This method, unlike some others, can be used with surfaces that are not homogeneous, for example deposition on trees and hedgerows can be assessed. Furthermore, it is possible to detect the sites of deposition, e.g. leaf cuticles or the lining of sub-stomatal cavities, but for this it is necessary to sample destructively.

$^{35}SO_2$ was used by Garland *et al.*, (1973) and Owers and Powell (1974). Krouse (1977) deduced sulphur deposition from an analysis of isotopic ratios of $^{34}S/^{32}S$. But care must be taken when extrapolating from deposits on isolated objects, e.g. plants in pots and single trees, because inputs may be unduly large as a result of the advection of polluted air from round about (the 'oasis' effect) and/or to through-flow of air past the object (the 'clothes-line' effect). Inputs to continuous canopies may be considerably smaller than to individual plants (Chamberlain, 1975*a*).

(3) Deposition in exposure chambers and cuvettes

Cuvettes, in which temperature, humidity and light can be controlled, are commonly used to study transfer of water vapour and carbon dioxide between plants and the atmosphere (reviewed by Jarvis and Catsky, 1971) but less frequently for exchanges of pollutants. In cuvettes it is desirable to achieve effective mixing to ensure that diffusion of pollutants to plant tissues is not restricted by large boundary layer resistances (Unsworth *et al.*, 1976). Deposition on plants in chambers or cuvettes may be assessed non-destructively by measuring the difference between gas concentrations entering and leaving the different types of chambers, or by destructively analysing plant material. In the former, non-destructive, method it is necessary to assess separately amounts of pollutant deposited on the walls of the chambers. Cuvette methods allow separation of cuticular deposition from stomatal uptake and so are useful in effects studies. With knowledge of canopy micrometeorology it is possible to extrapolate from cuvette results to estimates of canopy deposition, but this approach has seldom been attempted. Jarvis *et al.*, (1976) reviewed applications of the method for studying carbon dioxide uptake in forests. At the Workshop, Garland* described experiments (Garland and Branson, 1977) in which he exposed pine shoots, in a cuvette of the type used by Jarvis, to $^{35}SO_2$, and indicated how deposition of SO_2 on the forest could be estimated from his results. Richter* described a cuvette system designed for continuous non-destructive measurements of SO_2 deposition on conifers and Horntvedt* described exposure chamber studies of SO_2 deposition on spruce seedlings.

(b) Particles

The principles controlling the deposition of particles and droplets have been reviewed by Chamberlain (1975*a* and 1975*b*). Theory suggests that particle size is the most important factor determining the efficiency for particle capture by different surfaces; other factors include wind speed and surface configuration. As far as very small particles ($\sim$0.1 μm diameter) are concerned the trapping efficiencies of rough surfaces are much greater than those of smooth surfaces (Chamberlain, 1975*a*). Irrespective of the nature of the different surfaces larger particles may bounce off vegetation at high wind speeds unless the particles themselves or the surfaces are wet or sticky. These theoretical speculations have been generally supported by the results of laboratory experiments in which isolated vegetation elements and simulated canopies were exposed in wind tunnels. These experiments showed that the deposition velocities of sub-micron particles, typical of pollutants, were small: others indicated that deposition velocities differed with different plant species (Belot and Gauthier, 1975; Little and Wiffen, 1977). Wiman* described experiments in wind-tunnels in which particles with metal tracers were deposited on vegetation. Analyses by proton-induced X-ray emission (PIXE) and with a scanning electron microscope with energy-dispersive X-ray analysis were very sensitive for particles down to sub-micron range.

Experiments with sub-micron particles do not appear to have been done in forests. Wesely *et al.* (1977) recently described a new eddy correlation method for measuring fluxes of particles to short grass; their results indicate

much larger deposition velocities than are generally accepted. More commonly, deposition in the field is determined by linking deposits on aerial plant structures with atmospheric concentrations. Concentrations of airborne particles are usually assessed with cylindrical rods or threads of known impaction efficiencies, or suction samplers (May *et al.*, 1976).

(c) Wind-blown fog and mist

Vegetation captures large particles e.g. drops of fog and mist, relatively efficiently. Consequently, inputs of acidic wind-blown fog and mist to forests may be important in coastal and mountainous regions (Unsworth*). Although pollutant inputs by fog and mist do not seem to have been assessed, amounts of fog captured by forests were measured by Huzioka *et al.*, (1953, reviewed in Chamberlain, 1975*b*), using micrometeorological techniques: there are also numerous hydrological studies of fog inputs (reviewed by Rutter, 1975 and Penman, 1963). Unfortunately, it is difficult to obtain representative measurements of fog inputs because (i) capture efficiency of vegetation is strongly dependent on the size and distribution of leaves, and (ii) collection by dominant trees in a forest will be much larger than by surrounding smaller trees (an inverse 'clothes-line' effect) (Stewart*). A theoretical model recently proposed by Shuttleworth (1977) may be used as a basis for estimating inputs of fog and mist.

2. LONG-TERM METHODS

Several methods used in short-term studies may be applied in the longer-term, but they usually do not distinguish between gaseous, particulate and droplet inputs.

(a) Mass balance

This method generally requires the measurement, over long periods (usually weeks or more), of input, output and storage terms; gaseous and particulate inputs being calculated by difference, as has been done in the Hubbard Brook catchment study (Likens *et al.*, 1977). It is applicable to individual plants and to catchments, and has the added advantage of integrating over time and space when dealing with heterogeneous vegetation. Three participants (Roberts*; Horntvedt*; Bjor*) described their mass balance experiments.

(b) Isotope ratio

Plants grown in soil labelled with radioactive ^{35}S may be analysed after several weeks, when the isotope ratio ($^{35}S/^{32}S$) in plant tissues enables quantities of gas (SO_2) absorbed from the atmosphere to be deduced. This method has been used by Olsen (1957), Bromfield (1972) and Unsworth* On some occasions externally deposited SO_2 may be separated from internal uptake by carefully removing the former by washing.

3. TOPICS NEEDING FURTHER STUDY

(a) Development of short-term methods for measuring gaseous inputs to forests.

Of the micrometeorological methods, eddy correlation seems to be the most promising; disadvantageously the energy balance method demands very great precision (Stewart*; Galbally*; Garland*). Cuvette methods, combined with knowledge of canopy structure and micrometeorology, have potential (Garland*; Richter*). Models (e.g. Belot *et al.*, 1976) may be of value for aiding the estimation of inputs to heterogenous vegetation.

(b) Development of methods for studying physiological and chemical factors controlling the uptake of gaseous pollutants by plants.

More needs to be known about the chemical nature of plant surfaces and how this affects the deposition of pollutants, particularly when leaf surfaces are (i) wet (Fowler and Unsworth, 1974; Brimblecombe, 1978), or (ii) damaged by particles or acid rain (Fowler*; Unsworth*; Stewart*; Huttunen*). The duration of surface wetness in forests needs to be clarified.

(c) Processes affecting the deposition of sub-micron particles to plant (forest) canopies.

Wiman's sensitive methods might be exploited.

(d) Characterisation of the quantity and chemical quality of mist and fog captured by forests.

As a useful first step, droplet sizes and composition should be checked (Unsworth*; Stewart*).

(e) Effects of acid rain on the rates at which plants take-up gaseous pollutants

(see Evans *et al.*, 1977; also Huttunen*).

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E. SUBJECT AREA: THROUGHFALL AND STEMFLOW*

I. A REVIEW

by

B. Ulrich and R. Mayer

After falling onto forest canopies, precipitation becomes allocated to three fractions, (i) 'interception', (ii) throughfall and (iii) stemflow, the degree of partitioning depending upon amounts of precipitation, their distribution in time and the age and composition of the different forests. Thus, *c.* 123mm of stemflow were collected annually from beech (*Fagus sylvatica*), 125 yrs-old, but none from Norway spruce (*Picea abies*) 85 yrs-old (Table 1).

	Beech *Fagus sylvatica* A	Norway spruce *Picea abies* B	A – B
Precipitation (N)	1066 ± 295		
Throughfall (Kr) } (BN)	741 ± 232	764 ± 271	– 23
Stemflow (St) } (BN)	123 ± 26	0	123
Interception (I)	202 ± 51	302 ± 33	–100
Evapotranspiration (ET)	281 ± 33	316 ± 51	– 35
Seepage (Se)	551 ± 307	450 ± 299	101

Table 1. Effects of different tree species on the partitioning of precipitation at Solling *(mm, mean 1969 to 1972; ±, standard deviation)*.

During most of the year, interception losses are greater from spruce than beech (Table 2), interception implying the loss by evaporation of some of the precipitation that had earlier wetted aerial plant surfaces. This loss inevitably concentrates the solutes in the remaining water (viz. throughfall and stemflow) and hence the cycles of wetting may significantly affect the interplay between plant surfaces and atmospheric pollutants.

1. MODES OF DEPOSITION

Meteorologically, it is possible to distinguish between wet deposition (or wet precipitation), the sum of rain-out and washout (Georgii, 1965), and dry deposition (the sum of dry precipitation, plant filtering and soil filtering). Atmospheric inputs to terrestrial ecosystems include:

(a) Precipitation

(1) wet precipitation (rain, snow and mist),
(2) dry precipitation (dust, particles with diameters larger than *c.* 20 μm)

(b) Plant filtering

(1) assimilation of gases within plant tissues,
(2) solution of gases in water films adhering to plant surfaces with subsequent chemical reactions
(3) trapping of submicron aerosol particles carried to plant surfaces by wind.

(c) Soil filtering

(1) solution of gases in soil water (water films surrounding air-filled pore space) with subsequent chemical reactions,
(2) adsorption of aerosols and gases by soil particles.

2. CANOPY LEACHING

Leaching is regarded as the extraction of substances from leaves, stems and other aerial structures by water (Mann and Wallace, 1925; Wallace 1930), and, at one time, it was assumed to be an active process (Arens, 1934; Lausberg, 1935). However, this assumption has not been verified (Engel, 1939, Thorne, 1954; Schoch, 1955).

As demonstrated by Rouschal and Strugger (1940), the cell walls of parenchymatous tissues contain dissolved salts. Because it can occur from plant surfaces irrespective of the presence of stomata (Tukey, 1970), leaching may be interpreted as the diffusion of dissolved salts from cell walls to surface water films on leaves, the rates being controlled by concentration gradients. Some of the salts may be deposited on transpiring surfaces subsequently to be dissolved when leaves are wetted. Mecklenburg *et al.* (1966) and Yamada *et al.* (1966) have indicated that cations bound on acidic groups in cell walls may be exchanged, for example by H^+ ions, the time limiting step being diffusion. Thus, H^+ ions disappear from leaching solutions because they react with foliar substances. This sort of buffering was also found in throughfall collected beneath beech at Solling.

* References to Workshop contributions are marked with askerisks*

Month		N mm	BN mm	ET mm	Se mm	R mm	Sn mm	I mm	I as % of N	(I + ET) mm	(I + ET) as % of N
January	B	66.1	58.3	3.1	35.4	14.6	5.3	7.8	11.8	10.9	16.5
	NS		60.3	6.2	35.4	9.6	9.3	5.8	8.8	12.0	18.2
February	B	86.6	70.1	2.8	48.1	−3.4	22.5	16.5	19.1	19.3	22.3
	NS		63.4	5.6	39.5	−1.7	20.0	23.2	26.8	28.8	33.3
March	B	81.6	74.0	3.1	48.2	11.7	11.0	7.6	9.3	10.7	13.1
	NS		63.9	4.6	45.2	10.6	3.5	17.7	21.7	22.3	27.3
April	B	115.1	103.0	3.0	136.4	14.8	−51.3	12.1	10.5	15.1	13.1
	NS		101.1	10.3	116.8	5.2	−31.3	14.0	12.2	24.3	21.1
May	B	97.1	72.8	7.7	75.0	−4.9	−5.0	24.3	25.0	32.0	33.0
	NS		62.0	46.7	43.3	−16.8	−11.3	35.1	36.1	81.8	84.2
June	B	133.7	104.1	53.5	51.2	−0.5		29.6	22.1	83.1	62.1
	NS		92.1	45.1	36.7	10.3		41.6	31.1	86.7	64.8
July	B	83.2	63.8	74.2	29.9	−40.2		19.4	23.3	93.6	112.5
	NS		54.3	59.5	35.4	−40.6		28.9	34.7	88.4	106.3
August	B	105.6	81.8	57.8	18.5	5.5		23.8	22.5	81.6	77.3
	NS		69.7	52.1	20.3	−2.6		35.9	34.0	88.0	83.3
September	B	59.4	42.9	54.3	9.0	−20.4		16.5	27.7	70.8	119.2
	NS		35.4	35.8	10.5	−10.8		24.0	40.4	59.8	100.7
October	B	75.5	63.8	21.6	29.5	12.7		11.7	15.5	33.3	44.1
	NS		56.3	25.5	24.5	6.3		19.2	25.4	44.7	59.2
November	B	104.3	85.0	0.0	43.3	31.8	9.8	19.3	18.5	19.3	18.5
	NS		68.1	14.8	28.9	18.0	6.5	36.2	34.7	51.0	48.9
December	B	57.8	44.8	0.0	26.0	15.8	3.0	13.0	22.5	13.0	22.5
	NS		37.8	9.3	14.0	16.0	−1.5	20.0	34.6	29.3	50.7

N = precipitation; BN = throughfall + stemflow; ET = evapotranspiration; Se = seepage;

R = change in soil storage; Sn = change in snow storage; I = interception.

Table 2. Mean monthly components of water balances of beech (B), ***Fagus sylvatica*** and Norway spruce (NS), ***Picea abies*** forests at Solling *(Benecke and Ploeg, unpubl.)*.

Plant leachates from aerial structures usually contain substantial amounts of soluble organic matter (Tukey and Morgan, 1962; Bruckert *et al.*, 1971), up to 86 kg ha^{-1} monthly under oak (*Quercus petraea*) (Carlisle, 1965), with large amounts of soluble carbohydrates during some months of the year. Although leachates contain small amounts of nitrogen, most of the N is in the organic fraction (Tarrant *et al.*, 1968). Characteristically, cations and anions are not usually present in exactly equivalent amounts, the discrepancy possibly being explained by the presence of dissociated organic bound OH groups in organic acids or phenols (Table 3). According to Horntvedt*, more organic carbon is lost as the pH of the leaching solution is decreased.

At Solling, the difference between SCAT (cation equivalent sum) and SAN (anion equivalent sum) corresponds to 5% of SCAT in precipitation, 2% of SCAT in throughfall and −12% of SCAT in stemflow collected beneath beech at Solling (Table 4). The surplus of anions in stemflow disappears if N_{org} is assumed to carry a zero charge (OH groups are not dissociated at low pH). Silicic acid (not determined) should not be dissociated at pH < 4.2 and carbonic acid should be absent. The anionic character of organic substances in leachates needs more investigation, although the leaching of salts does not need to be causally connected with the leaching of organic metabolites. The factors influencing leaching are discussed by Tukey and Morgan (1964).

I. Cation equivalent sum (SCAT)

Flux	Time of year[a]	SCAT (eq. $ha^{-1}yr^{-1}$)	% of SCAT								
			H^+	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	Mn^{2+}	Al^{3+}
Open field precipitation (N)	Sr	1310	27	25	7	4	20	5	1	6	5
	W	1580	25	25	16	3	17	6	1	3	4
Throughfall (Kr)	Sr	1860	13	13	7	19	28	7	6	4	3
	W	2110	27	18	16	6	21	6	1	1	4
Stemflow (St)	Sr	627	25	9	6	22	19	5	7	3	4
	W	859	37	7	16	10	18	6	1	2	3

II. Anion equivalent sum (SAN)

Flux	Time of year[a]	SAN (eq. $ha^{-1}yr^{-1}$)	% of SAN				
			NO_3^-	Cl^-	PO_4^{3-}	SO_4^{2-}	N_{org}^-
Open field precipitation (N)	Sr	1310	18	11	0.7	53	17
	W	1480	18	23	0.6	50	8
Throughfall (Kr)	Sr	1770	15	13	0.6	53	18
	W	2130	14	22	0.3	51	13
Stemflow (St)	Sr	668	6	10	0.01	68	16
	W	1010	6	17	0.01	65	12

[a] Sr = May to October; W = November to April

Table 3. The cation (SCAT) and anion (SAN) equivalent sums in precipitation, throughfall and stemflow at a beech ***(Fagus sylvatica)*** stand at Solling.

Flux	Months of observations	pH	SCAT[b] (A)	SCAT − SAN (B)	(B) as % of (A)
Precipitation	73	4.1	241	+12	+ 5%
Throughfall	73	4.0	331	+ 6	+ 2%
Stemflow	64	3.4	124	−15	−12%

[b] eq. ha^{-1} mo^{-1}

Table 4. The difference between cation equivalent sums (SCAT) and anion equivalent sums (SAN) when analysing precipitation, throughfall and stemflow at a stand of beech ***(Fagus sylvatica)*** at Solling.

3. ASSESSMENT OF DEPOSITION

(a) Total dry deposition

Fowler* described a micrometeorological method for short term measurements (time scale: hours) of dry deposition (Garland, 1974; Fowler and Unsworth, 1974), whereas Bolin and Persson (1975) and Slinn (1977) exploited a macrometeorological approach giving annual mean values, regionally differentiated for parts of western Europe. Bolin and Persson estimated that the wet deposition of S in central parts of western Europe amounted to 20 to 40 kg S $ha^{-1}yr^{-1}$, with similar amounts being attributed to dry deposition (Slinn, 1977).

Garland *et al.* (1973) and Owers and Powell (1974) have used radio-labelled SO_2 in short experiments (time scale: minutes) whereas others who have been concerned with the longer term annual fluxes have favoured mass balances on a catchment scale. However, this seemingly simple approach is fraught with difficulties, e.g. problems involved with estimations of (i) vegetation and soil storage, and (ii) transfers between bedrock and interstitial water particularly if the rock is being actively weathered.

(b) Entry of gaseous pollutants into surface films and the capture of aerosols

The entry of gases into films of moisture on plant surfaces and the capture of aerosols transported to surfaces by wind are very difficult to separate. In the Solling project, the greater dry deposition of S in winter than in summer was associated with increasingly acid stemflow and throughfall so indicating the importance of the direct absorption of SO_2. Perhaps fortuitously, the ratios of wet deposition to dry deposition were the same for Na, Ca, Mg and Cl as for S (Ulrich and Mayer*). But, whereas the dry deposition of sulphur relates to the transfer of gaseous SO_2, that of the other elements would be largely attributable to the capture of aerosols.

(c) Plant filtering

Plant filtering = throughfall + stemflow − precipitation assuming that gas assimilation and other sources and 'sinks' are unimportant (Miller, 1963). In reality, the products of leaching form an important additional 'source' of some substances, whereas leaf uptake ('gas assimilation'), as for NH_4^+, and the formation of precipitates (notably of Fe and heavy metals) on leaves may effectively act as 'sinks'.

To calculate dry deposition for the summer months Mayer and Ulrich (1974) assumed that the increased content of throughfall and stemflow during the winter leafless period was attributable to dry deposition, and that the ratio of precipitation to 'plant filtering' would remain the same irrespective of season. To simulate plant filtering White and Turner (1970) designed an artificial impactor.

(d) Soil filtering

Soil filtering = seepage + runoff − precipitation.
This equation, which, like that for plant filtering, assumes that other sources and sinks are unimportant, can be solved by the mass balance approach (Bromfield and Williams, 1974), but, because of widely varying amounts of precipitation and seepage, it is only possible to obtain meaningful results using yearly means.

The estimation of soil storage poses analytical problems. In some conditions, soil, by the mineralization of organic S, may act as a source of S. In other (notably acidic) conditions, soil, by forming aluminium sulphates, may act as a sink.

Over a period of six years, Kühn and Weller (1977) estimated that 'precipitation' at a site in Central Europe provided 29 kg S $ha^{-1}yr^{-1}$, and that the filtering effect of bare soil accounted for 12 to 20 kg S $ha^{-1}yr^{-1}$. In contrast, the filtering effect of a stand of beech at Solling *viz.* 26 kg S $ha^{-1}yr^{-1}$ (precipitation, 24 kg S $ha^{-1}yr^{-1}$) was appreciably greater, suggesting that rates of dry deposition on beech are greater than on a bare crumby soil. This result is in accord with differences in surface roughness (Slinn, 1977), but other factors, e.g. the chemical nature of the differing surfaces, may be equally important. It seems that deposition in a structured forest is confined almost exclusively to the canopy formed by the overstorey.

4. ASSESSMENT OF LEACHING

When spruces, 8 years-old and growing in acid soil within a sealed chamber supplied with filtered air, were sprinkled with rain, the amounts of K and Mn in throughfall were found to be significantly greater than in the original rain (Table 5), so duplicating field observations made at Solling (Ulrich and Mayer*).

	Incident precipitation (A)	Throughfall (B)	B/A
pH	5.1	5.4	–
Solutes (mg m^{-2})			
H	0.1	0.05	0.5
Na	23.1	13.4	0.5
K	2.4	13.5	5.7
Ca	10.2	11.9	1.2
Mg	3.5	2.9	0.8
Fe	0.2	0.2	1.0
Mn	0.04	0.4	10.0
Al	0.04	0.05	1.2
N	7.3	10.0	1.4
S	26.7	21.9	0.8

Table 5. The different chemistry of incident precipitation and throughfall collected beneath Norway spruce ***(Picea abies).***

Miller *et al.* (1976) based their approach upon independent estimates of dry deposition onto rain gauges. They argued that an increase in the chemical content of throughfall and stemflow attributable to 'plant filtering' should be related to 'dry deposits' accumulating on these gauges. With this assumption the intercept, when plotting 'gauge' dry deposition against 'plant filtering', gives an estimate of leaching.

At Solling, the problem has been argued using the monthly SO_4-S fluxes in precipitation, throughfall, stemflow and seepage (Fig. 5). The SO_4-S fluxes in precipitation remained more or less constant throughout the year but those in throughfall and stemflow were augmented from September to March. Remembering the deciduous nature of beech, the increased concentrations from November to March cannot be attributed to foliar leaching, but are related instead to dry deposition of SO_2 whose atmospheric concentrations are enhanced during winter (because of domestic heating). However, during September and October, and before the onset of winter domestic heating, the increased sulphur fluxes in throughfall and stemflow are probably a reflection of the more effective leaching of senescent, than of green active, leaves (Denayer de Smet, 1962; Miller, 1963). It is suggested that the difference in the SO_4-S fluxes in throughfall and stemflow collected from September to October and from May to August gives an estimate of the quantitative effects of leaching. From 1968 to 1976, 'leaching' from beech at Solling amounted to 3.4 kg $SO_4-S\ ha^{-1}yr^{-1}$ but with a very substantial error term (Table 6).

In other comparative tests, it seems that the enrichment of throughfall and stemflow at Solling with K and Mn may be almost completely attributable to leachates, with the leaching of all other elements being of minor importance, always accepting that there may be large seasonal differences related to the onset of senescence.

5. RELATION BETWEEN VOLUMES OF THROUGH-FALL AND STEMFLOW AND SOLUTE CONCENTRATIONS

As indicated by Ulrich and Mayer*, the concentrations of different elements in throughfall and stemflow are influenced by the volumes of throughfall and stemflow. This effect is particularly noticeable when analysing individual rain events, and is still discernible when considering monthly means.

6. SAMPLING PROCEDURES

Different types of errors and variations can be distinguished:

	Precipitation (N)	Throughfall (Kr)	Stemflow (St)	Kr + St (BN)	Leaching (PA)	Canopy filtering (Fi)	Soil input (BI)	Seepage (Se)	Change in soil storage (R)
1968/69	24.8	42.3	28.2	70.5	3.6	42.1	73.7	nd	nd
1969/70	26.9	40.2	12.5	52.7	5.2	20.5	55.9	46.3	0.6
1970/71	19.7	24.8	10.2	35.0	0	15.3	38.2	22.4	12.1
1971/72	23.6	35.9	12.3	48.2	0	24.6	51.4	24.8	22.9
1972/73	21.6	27.9	16.2	44.0	4.9	17.6	47.2	nd	nd
1973/74	22.9	35.0	21.3	56.3	10.6	22.8	59.5	nd	nd
1974/75	28.0	31.8	32.3	64.1	2.1	34.0	67.3	51.4	10.1
1975/76	23.0	39.8	14.3	54.1	0.4	30.6	57.3	nd	nd
Average	23.8	34.7	18.4	53.1	3.4	25.9	56.3	36.2	11.4[(c)]

Fi (canopy filtering) = BN − (N + PA)

BI (soil input) = BN + L; where L = litterfall of 3.2kg S $ha^{-1}\ yr^{-1}$.

R (changes in soil storage) = N + Fi − (Se + P); where P = annual biomass increase of 0.5kg S $ha^{-1}\ yr^{-1}$.

nd, not determined.

(c), 13.0 when calculated from the averages of N, Fi and Se.

Table 6. Annual flux of SO_4-S in a stand of beech ***(Fagus sylvatica)*** at Solling from 1968 to 1976 (flux balance kg $SO_4-S\ ha^{-1}\ yr^{-1}$).

(i) Contamination of rainfall, throughfall and stemflow by substances released from collection vessels.
(ii) Contamination of rainfall, throughfall and stemflow by substances accumulating on collectors during dry periods.
(iii) Contamination by birds, insects etc.
(iv) Utilisation of solutes by algal contaminants.
(v) Utilisation of solutes by microbes (e.g. nitrification).
(vi) Concentration changes attributable to litter accumulations.
(vii) Concentration increases consequent upon evaporation.
(viii) Different sensitivities of different analytical procedures.

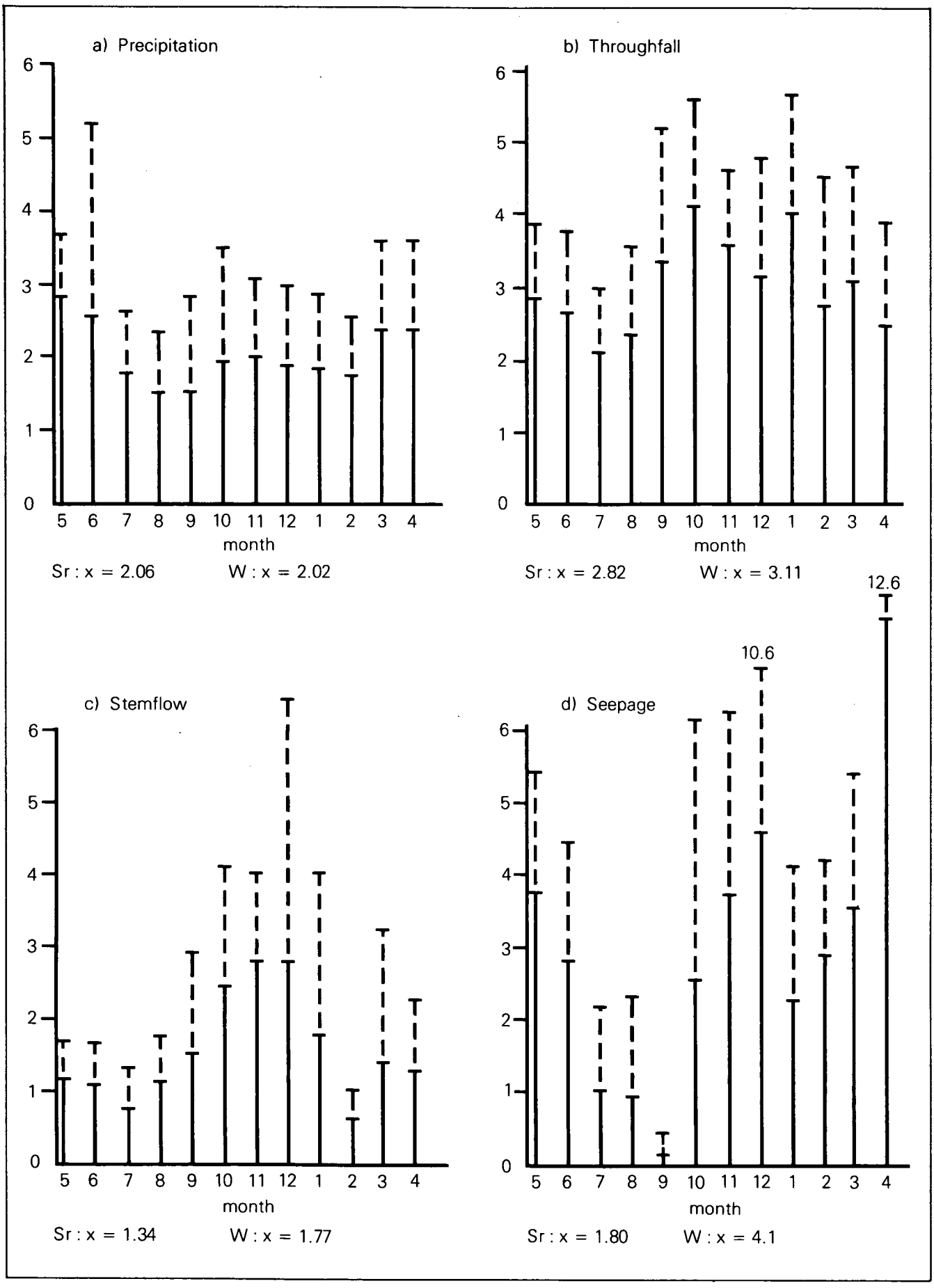

Fig. 5. Monthly mean values (kg ha^{-1}) of SO_4^{2-} in precipitation, throughfall, stemflow and seepage in a stand of beech ***(Fagus sylvatica)*** at Solling. Sr : x = summer mean, W : x = winter mean. (Broken vertical lines indicate standard deviations between years)

(ix) Differences attributable to variations occurring naturally at different locations within a forest or vegetation assemblage.
(x) Differences attributable to the selection of different trees for study.
(xi) Sample partitioning for stemflow.

While some of these problems are difficult to overcome, others, particularly those concerned with replicate sampling procedures can be minimised by appropriate statistical procedures (Kimmins, 1973). In the Solling project, 5 locations have been sampled on each of 3 transects when assessing throughfall, whereas 3 trees of different sizes (diameter at breast height) were used for stemflow studies. In determining the concentration of solutes in throughfall, there was a coefficient of variation of up to 40% which reached 80% when analysing stemflow. These errors could be lessened by increasing numbers of replicate samples and/or by increasing the run of data. If the latter option were preferred, observations would have to be taken for at least 5 and 20 years respectively if the mean concentrations of solutes in throughfall and stemflow were to have an error of ± 10%. This type of problem is relatively easily resolved, but, at a more fundamental level, it is necessary to decide the sampling strategy needed to obtain accurate assessments of the average chemical compositions of throughfall and stemflow, remembering that concentrations are likely to change in a systematic manner during rain episodes of different durations and intensities. But, is it desirable and necessary to collect samples separately for each rain event? Can these be used to obtain weighted means by making allowances for different volumes and concentrations? Is the relation between volumes and concentrations close enough to enable worthwhile predictions to be made?

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E. SUBJECT AREA: THROUGHFALL AND STEMFLOW*
II. THROUGHFALL, STEMFLOW, CROWN LEACHING AND WET DEPOSITION: CHAIRMAN'S REPORT AND RECOMMENDATIONS

by
H.G. Miller

At an early stage of ecological research it is desirable to find the balance most appropriate to the study's objectives, between precision of individual measurements and numbers of measurements. As objectives change from study to study, methods must also change. It follows, despite the vigour with which some promote their own methods, that there can be no single technique appropriate to all circumstances; indeed, the promulgation of standard techniques may even impair future progress. However, because the experience of others can be helpful to those newly entering a field of research it was decided to prepare the following compendium.

1. GROSS PRECIPITATION

(a) Sampling intensity

As gross rainfall can vary over fairly short distances, several gauges may be needed to obtain reasonable estimates, the number of gauges increasing rapidly with each increase in the desired level of precision. If a large area is to be sampled, consideration should be given to stratifying it by topographic features such as altitude and aspect (Rodda, 1970), particularly if water quality is to be assessed on samples from only a proportion of the total number of gauges deployed.

(b) Design of gauge

Errors resulting from evaporation, splash-out and similar causes are usually minimized by (i) rain-gauge design (Bleasdale, 1959), and (ii) by field maintenance (Mellanby, 1976). The standard gauge has been widely used but it is subject to several sources of error, notably wind turbulence. The most representative measurements are probably obtained with ground-level gauges, each with its orifice at ground level and surrounded by a honeycomb, or slatted surface, that prevents splash (Rodda, 1970). For forested areas, it has been suggested that gauges, surrounded by some form of aerodynamic screening (Nipher, 1878; Allis *et al.*, 1963; Reynolds and Leyton, 1963; Corbett, 1967), should be mounted above the canopy (Rowe and Hendrix, 1951; Pereira *et al.*, 1962). Recent evidence suggests that when the amount of snow is not important, canopy-level gauges give results very similar to those obtained with ground-level gauges (Newson and Clarke, 1976) but that, when snow is a major factor, it may be necessary to use additional bucket-type snow samplers (Galloway and Likens, 1976). Gauges that are closed except during rain are being used in some studies, but it seems unlikely that these will make the interpretation of results much easier.

* Reference to Workshop contributions are marked with askerisks*

2. THROUGHFALL

(a) Sampling Intensity

The enormous spatial variation in throughfall beneath a forest canopy necessitates a large number of gauges (Kimmins, 1973). If there is prior knowledge of a pattern of variation associated with identifiable features of the structure of the canopy, or if topography varies appreciably across the site, stratified random sampling should be considered. The number of gauges required can be reduced by using a system of roving gauges (Wilm, 1946; Attiwill, 1966; Rieley *et al.*, 1969), and the results perhaps adjusted by covariance on gross rainfall. Helvey and Patric (1965) concluded that twenty gauges used in this manner 'should suffice for most study objectives'. Randomly-moved gauges have the advantage of giving an increasingly better long-term sample, as the different random errors are summed (Stewart*).

(b) Design of gauge

In an attempt to decrease sampling error, systems of troughs or plastic sheets have been used (Grunow, 1965; Calder and Rosier, 1976). These can be effective, but may introduce excessive 'wetting-up' errors; they are easily blocked by leaf litter and produce large volumes of water (Stewart*). Furthermore, there may be problems in obtaining sufficient fall from the head of the collector to the collecting bottle. For these reasons most investigators have used gauges of the standard funnel-type design (e.g. Miller, 1963; Carlisle *et al.*, 1966; Nihlgård, 1970; Foster and Gessel, 1972; Eaton *et al.*, 1973; Miller and Miller, 1976.).

3. STEMFLOW

(a) Sampling intensity

Because amounts of stemflow per tree are closely related to basal area (Wicht, 1941; Rutter, 1963), sample trees should be stratified by basal area. Numbers of trees to be fitted with stemflow gutters depend on the relative contribution of stemflow to the net rainfall reaching the soil surface. This contribution is a function of species, but, within any one species, it tends to increase with increasing gross rainfall and decreases with increasing crop height (Miller*).

(b) Design of gauge

Gutters are usually coiled in a helix around stems at about breast height. They should be made of material that stretches as trees grow. Aluminium (e.g. Voigt, 1960; Weetman, 1962; Rutter, 1963) and lead (e.g. Wicht, 1941; Carlisle *et al.*, 1967; Miller *et al.*, 1976*a*) have both been used, as has rubber (Mina, 1965; Nihlgård, 1970), but polyurethane, (possibly moulded directly onto stems) (Olson, 1968; Likens and Eaton, 1970), or preformed gutters of vinyl moulding com-

pound (Miller and Miller, 1976) are preferable. The gutter can be cushioned against the tree with fibreglass (Voigt, 1960), plastic filler (Carlisle *et al.*, 1967), rubber (Nihlgård, 1970), asbestos bitumen putty (Miller *et al.*, 1976*a*) or builders' mastic (Miller and Miller, 1976), and sealed with a coat of non-contaminating paint. In forming the gutter, the breadth of the opening should be kept narrow to reduce the chance of collecting leaf litter.

A considerable amount of water can flow down a single tree, even over fairly short periods. This means that either a very large container must be used or some system of automatic volume measurement with a sample-splitter has to be installed (White and Rhodes, 1970; Miller and Miller, 1976). Whichever approach is used there can be problems in obtaining sufficient fall from the gutter to the sample container unless the latter is sunk into the ground.

4. CONTAMINATION

(a) Materials

It is important that the materials used should neither introduce contaminants nor promote catalytic reactions. Resistance glass (e.g. Pyrex and Jena), stainless steel (e.g. British Standards Institution, 1969; World Meteorological Organisation, 1974), and plastics (notably polyethylene and polypropylene, both of which are suitable and convenient) are frequently recommended. However, fillers are incorporated into many plastics during manufacture and these may be a source of contamination. All materials, therefore, should first be tested to check for the release of contaminants when wetted with slightly acidified water. It is known that zinc, which is used in standard rain gauges, can promote catalytic conversion of nitrate to ammonia (Egnér *et al.*, 1949) and for this reason metals other than stainless steel should be avoided. Similarly, contact with rubber is best kept to a minimum. Containers should be cleaned as frequently as possible and new bottles, particularly if made of Pyrex, should be thoroughly cleaned before use (Egnér *et al.*, 1956).

(b) Insect frass, bird droppings and other solids

Contamination of this sort is likely to be most severe in, but by no means limited to, throughfall gauges. It is advisable to plan for a certain degree of over-sampling so that results from contaminated gauges can be rejected (Miller*). Single samples with aberrantly large concentrations of nitrogen, phosphorus or calcium should be treated with suspicion (e.g. acidified bones in owl pellets can give large amounts of phosphorus and calcium). The risk of birds perching on gauges can be greatly reduced by surrounding gauges with rings of vertical spikes (Egnér *et al.*, 1949) or with circumferential bird guards such as those recommended by the British Standards Institution (1969) and by the Norsk Institutt for Luftforskning (1976).

(c) Leaf fall

All gauges should have filters to prevent fallen leaves being washed into the storage containers. Filters that have been used include cotton wool (Will, 1959), gauze (Carlisle *et al.*, 1966), a fine mesh of plastic (Foster and Gessel, 1972) or stainless steel (Attiwill, 1966) and filter paper (Madgwick and Ovington, 1959 ; Eaton *et al.*, 1973; Miller and Miller, 1976).

(d) Soil splash

Gauges should be at a height sufficient to minimize the chances of contamination by soil splash. This height will vary between sites, but is unlikely to be less than 0.35m. An estimate of contamination can be obtained by analysing water for total aluminium and other substances commonly occurring in soil (Freedman*).

(e) Gaseous adsorption

Some materials used in making rain gauges readily adsorb sulphur dioxide or ammonia from the atmosphere. The significance and importance of this phenomenon is not, as yet, fully explored.

5. CHANGES BEFORE ANALYSIS

(a) During the collection period

Losses of some elements, notably phosphorous, can be very large. Algal and bacterial growth can be minimized by rapidly chanelling the sampled water into clean and darkened containers, and by replacing these containers at frequent intervals. 'Growths' can also be decreased by adding preservative compounds such as the moderately effective pentachlorophenol and hexachlorophane; other preservatives (notably chloroform, toluene and alcohol) appear to be of little value (Allen*). A saturated solution of mercuric chloride is usually very effective as a preservative, but care is needed because of its toxic properties and because it may interfere with subsequent chemical analyses. At all events, samples should be left in the field for the shortest possible time, preferably less than one, and certainly no longer than two, weeks.

(b) During storage

Storage at $-15°C$ appears to be safe and convenient, but analyses must be done soon after thawing as the freeze-thaw action accelerates biological activity (Allen*). However, as rainwater samples usually have a fairly low pH, it seems likely that they can be stored in the dark at higher temperatures for fairly long periods (Roberts and Clarke*). Galloway and Likens (1976) found that, apart from PO_4^{3-} and Cl^-, there is no change in chemical composition after storage for seven months at temperatures in the range $+4°C$ to $-4°C$.

6. INTERPRETATION OF RESULTS

(a) Factors controlling acidity

Work in Scandinavia (e.g. Dovland *et al.*, 1976) and in western England (Roberts and Clarke*) has shown that the pH of rain water is related to sulphur deposition. However, this relationship appears to be weaker in areas closer to possible sources of contamination, such as the north-eastern United States (Likens and Bormann, 1974) and the Cracow region of Poland (Kasina*). The processes of acid formation and neutralization are not well understood, but it does seem clear that pH measurements alone do not adequately express the acidic nature of precipitation (Reuss, 1977; Krupa *et al.*, 1976). Thus, on the one hand, significant errors may result from changes in the partial pressure of atmospheric CO_2, particularly for samples above pH 5

(Reuss, 1977), whereas, on the other hand, the acidity at lower pH values will be controlled by a complex interaction of strong acids, weak acids and hydrolysable salts. The relative importance of strong acids and weak acids has been the subject of some argument, although generally it would seem that the strong acid component is dominant (Frohliger and Kane, 1975; Odén, 1976; Likens *et al.*, 1976; Galloway *et al.*, 1976). Strong acids include H_2SO_4 (largely derived from SO_2), HNO_3 (derived from oxides of nitrogen) and HCl (which can result from the reaction of sulphur dioxide and sea-salt) (Eriksson, 1960; Brosset *et al.*, 1975). These acids can be neutralized by ammonia or by alkaline substances in the form of carbonates and oxides (Junge, 1963), reactions that are most marked in the vicinity of emmission sources (Kasina*). As pH measurements are inadequate, the concentration of strong acids should be determined by potentiometric or coulometric titration (Askne and Brosset, 1972; Liberti *et al.*, 1972; Krupa *et al.*, 1976; Norsk Institutt for Luftforskning, 1976) or by determining the major anions and cations, other than H^+, and the hydrogen ion loading required to maintain electrical neutrality can be calculated (Reuss, 1977). Electrical conductivity is almost completely determined by the concentrations of SO_4^{2-}, Cl^-, NO_3^-, HCO_3^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, H^+ (World Meteorological Organisation, 1974). If, however, the pH is below 5.5, HCO_3^- would not be present; Reuss (1977) has also excluded Na^+, although its exclusion is not valid in coastal regions where large concentrations of sodium can occur.

(b) Excess sulphur

Comparison of ionic ratios in rainwater and sea water should not be made uncritically, as there may well be some ionic separation either during aerosol formation or at a later stage (e.g. Wilson, 1959; Sugawara, 1965; Granat, 1972; Chesselet *et al.*, 1972). However, at least in coastal regions, the ratio of sulphur to sodium or magnesium can be used to calculate "excess" sulphur (A. Semb, personal communication), originally defined by Eriksson (1960) as being the sulphur left after subtracting sea-salt particle sulphur. It is important to realize that this does not exclude the sea as a source of some of the excess sulphur; apart from changing ionic ratios there is the possibility of sulphur from sea-derived H_2S (Conway, 1942 *a* and *b*; Robinson and Robbins, 1970). Clearly then, it is dangerous to take the step from the premise 'anthropogenic sources contribute to excess sulphur', to 'excess sulphur is a measure of anthropogenic emission', without further information on the relative contribution from all sources.

(c) Element gain

Throughfall and stemflow gain soluble salts as a result of crown leaching and by washing elements, trapped from the atmosphere, from plant surfaces.The 'trapped' elements accumulate as a result of gaseous adsorption and of impaction of either dry or wet particles, including fine rainfall which may be grossly under-sampled by normal rain gauges. Furthermore, the extent of element gain can vary widely with changes in environmental factors, for example a change in pH of rain from 6 to 3 has been found to double concentrations of Ca, Mg, K and Mn in throughfall beneath Norway spruce (Horntvedt*). More information is needed, but it is crucially important to devise a means of separating gain into the input and crown leaching components. This problem is intrinsically difficult. Direct approaches include the monitoring of total catchments (e.g. Likens *et al.*, 1977) and measuring the catch of airborne particles on artificial impactors (e.g. White and Turner, 1970). In the first approach, it is very difficult to obtain accurate measurements of small changes in large zones of accumulation (e.g. the soil), and of the separate input through nitrogen fixation and adsorption of ammonia and sulphur dioxide by soil. In the second approach, uncertainty arises from the number and validity of the assumptions made in converting results for artificial impactors to areas of forest. More recently, two indirect techniques have been proposed. Mayer and Ulrich (1974 and 1977) suggested that the proportional gain in throughfall beneath beech during the leafless winter months could be used for separating crown leaching from input during summer, whereas Miller *et al.* (1976*a*) proposed a more generally applicable regression technique. The method developed by Mayer and Ulrich, which depends on a number of assumptions, is only suitable for deciduous trees and for elements for which stemflow is not a major pathway. The technique of Miller *et al.* is applicable to all species and is based on fewer assumptions, but one of these assumptions is that all forms of input (wet and dry deposition) can be treated as a single variable, and, should this assumption not hold in practice, the method would tend to overestimate crown leaching (Lakhani*) (see footnote). It also assumes that the extent of crown leaching is statistically independent of the extent of wet deposition.

7. DIRECTIONS FOR FUTURE WORK

(a) Separation of crown leaching and input

As described above, it is crucial that an unbiased and robust method be devised for separating crown leaching from input.

(b) Factors influencing crown leaching

More information is needed on the physiological and morphological factors controlling leaching of conifer needles, on the known variation with season (e.g. Miller *et al.*, 1976*a*), and on the response to environmental factors, notably to the acidity of rainwater (e.g. Abrahamsen *et al.*, 1976).

(c) Snow

There is very little information on the input of elements in snow, and none on crown leaching during periods of snow. As a large proportion of the total precipitation in some parts of the world occurs as snow, this is a serious omission.

(d) Stand structure

Most observations of wet deposition and the internal cycling of nutrients have been made on even-aged

Footnote See Lakhani, K.H. and Miller, H.G. (In press). Assessing the contribution of crown leaching to the element content of rainwater beneath trees. In Proc. NATO Conf. *Effects of acid precipitation on terrestrial ecosystems*. Toronto, 1978.

monocultures. There is a need to know more about these processes in other forest types, particularly in the extreme variant of a multi-layered forest with a diverse array of plant species with different configurations, as found in the natural forests of many tropical and sub-tropical regions.

(e) Chemistry of rain and snow water

More needs to be known about (i) the chemistry of precipitation and (ii) the mechanism of element insertion into the atmosphere. In particular, information is needed about natural sources.

(f) Dust

Almost all studies have been concerned with elements dissolved in rainwater. But, there is also a significant input of phosphate in dust (Tamm, 1958) and recent evidence from Canada (Freedman*) suggests that fairly large inputs of other elements are released from dusts even in relatively uncontaminated regions.

(g) Chemical transformations on tree surfaces

It is known that some of the phosphate in particles of calcium phosphate (an artificial fertiliser) trapped on tree foliage appears in soluble form within a few weeks (Miller*). No doubt many other elements may be similarly dissolved from dust trapped by trees, and transformations of adsorbed gases may also occur prior to their being washed from leaves. The significance of these transformations is virtually unknown.

(h) Significance of measured rates of input and crown leaching

An assessment is required of the physiological, ecological, pedological and evolutionary significance of atmosphere input and crown leaching in forests. It now seems that much of the element-gain, measured beneath trees, represents a net input to the site (Mayer and Ulrich, 1974), and that forests can conserve certain nutrients by maintaining a rapid cycle (Miller *et al.*, 1976*b*; Stone and Kszystyniak, 1977). Information enabling informed discussion of the significance of these processes in relation to the evolutionary adaptation of trees to soils of low nutrient status, to soil pedogenesis, to the succession of species, and to the reaction of different forest ecosystems to increasing pollution, is slowly becoming available.

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II LIST OF CONTRIBUTIONS
SUBJECT AREA: EVALUATION OF ATMOSPHERIC INPUTS

Chairman, M.H. Unsworth

Title of contribution	***Contributors***
Dry deposition of gases and particles onto vegetation: a review (POSITION PAPER)	*M.H. Unsworth*
Field measurements of SO_2 fluxes to vegetation and their interpretation	*D. Fowler*
Measurement of SO_2 uptake by the eddy correlation method	*I. Galbally*
Exposure chamber studies of SO_2 deposition on spruce seedlings	*R. Horntvedt*
Report on current Swedish studies of dry and wet sulphur deposition	*S. Linder* *J.E. Hällgren* *L. Granat* *A. Richter* *F. Anderson* (Reporter)
Deposition of $^{35}SO_2$ to pine needles	*J. Garland*
Deposition characteristics and physiological effects of particulates on plant surfaces (Part 1)	*F.A. Bazzaz* *R.W. Carlson* *J.J. Stukel*
An experimental approach to the plant-aerosol system	*B. Wiman*
Evaluation of loading of sulphate and heavy metals along an S-SE transect centring on Sudbury, Ontario	*B. Freedman*
Total input of acid substances to forest ecosystems	*P. Grennfelt*
The input of gaseous and particulate sulphur to a forest ecosystem	*J.S. Eaton*

SUBJECT AREA: THROUGHFALL AND STEMFLOW

Chairman, H.G. Miller

Title of contribution	*Contributors*
Throughfall and stemflow (POSITION PAPER)	*B. Ulrich* *R. Mayer*
Assessment of flux balance and amount of deposited chemical elements in a beech and a spruce forest in central Europe	*B. Ulrich* *R. Mayer*
Over-estimation of wet deposition of atmospheric sulphur due to dry deposition on collecting funnels	*D. Fowler*
Problems in the measurement of incident rain and throughfall in forest ecosystems	*J.B. Stewart*
Measurement of throughfall and stemflow in spruce plantations	*H.G. Miller*
Problems arising during the collection of rainwater	*S.E. Allen*
Methods in wet deposition research of sulphur compounds in the region of Cracow	*S. Kasina*
Evaluation of sulphate and heavy metal loading rates and total sulphation as affected by forest canopies near Sudbury, Ontario	*B. Freedman*
Leaching of chemical elements from tree crowns by acidified irrigation water	*R. Horntvedt*
Monitoring precipitation chemistry in the Merseyside area	*T.M. Roberts* *T. Clarke*
Assessing the contributions of crown leaching, rain and dry deposition to the chemistry of throughfall and stemflow	*H.G. Miller*

SUBJECT AREA: MEASUREMENT OF EFFECTS

Chairman, K. Bjor

Title of contribution	*Contributors*
Measurement of Effects (POSITION PAPER)	*K. Bjor*
Deposition characteristics and physiological effects of particulates on plant surfaces (Part 2)	*F.A. Bazzaz* *R.W. Carlson* *J.J. Stukel*
The measurement of biological effects of some gaseous air pollutants in local, regional and national monitoring networks in the Netherlands	*A.C. Posthumus*
Effects of smelter emissions on surrounding forest plant communities near Sudbury, Ontario	*B. Freedman*
A review of the methods used to investigate the effects of acid precipitation on microbial processes in forest soils	*P. Ineson* *T.M. Roberts* *T. Clark* *T.R.G. Gray*
The research project into the effects of air pollution (including acid rain) on the northern coniferous forests	*S. Huttunen*
Growth response to acid precipitation	*K. Bjor*
Ecosystem approaches to the effects of acid deposition on forest soils and forest growth	*F. Andersson*

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